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SCUOLA DI DOTTORATO DI RICERCA IN INGEGNERIA INDUSTRIALE
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CICLO XXIV

Materiali e rivestimenti innovativi per applicazioni biomedicali
(innovative coatings and materials for biomedical applications)

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Humanity needs practical men, who get the most out of their work, and, without forgetting the general good, safeguard their own interests. But humanity also needs dreamers, for whom the disinterested development of an enterprise is so captivating that it becomes impossible for them to devote their care to their own material profit.

Without doubt, these dreamers do not deserve wealth, because they do not desire it. Even so, a well-organized society should assure to such workers the efficient means of accomplishing their task, in a life freed from material care and freely consecrated to research.

Marie Curie (1867-1934)
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GENERAL INTRODUCTION

In the human body environment, most advanced materials and metallic alloys cannot be actually applied because of their composition, their chemical resistance or their mechanical characteristics. It is in fact well known that a wide number of chemical elements, and in particular Antimony, Arsenic, Barium, Beryllium, Cadmium, Hexavalent Chromium Cr\(^{6+}\), Lead, Mercury, Osmium, Thallium and Vanadium are considered toxic for the human body and thus their presence in prosthetic implants and/or temporary contact devices must be avoided. Other elements, such as Nickel may be responsible of inflammatory responses in sensitive and allergic patients. Aluminium has no biological role and its classification into toxic metals is controversial. Significant toxic effects and accumulation to tissues have been observed in renally impaired patients. However, individuals with healthy kidneys can be exposed to large amounts of aluminium with no ill effects. Recently, Haltzaimer syndrome has been correlated with elevated amounts of aluminium deposited in the brain. Most other elements may have toxic effects when their concentration exceeds certain values, such as Iron, Zinc, Copper and Fluorine. For this reason, only a limited array of materials are actually applied for the production of biomedical components.

The main biomedical applied metallic alloys are:

- **AISI 316L and 316LVM Stainless Steels.** Because of its excellent corrosion resistance coupled with good mechanical resistance, 316 is widely used for surgical implants (both temporary and permanent) and instruments, medical devices and equipment;

- **AISI 630 Stainless Steel.** A good compromise between corrosion and mechanical resistance, AISI 630 is often used for instruments and temporary contact equipment;

- **AISI 420 Stainless Steel.** Thanks to its good mechanical resistance and average corrosion resistance, AISI 420 is often used for surgical blades;

- **CoCrWNi (F90), CoNiCrMo (F562).** Cobalt alloys are used for tribological behaviour and high corrosion resistance, even if their density and young modulus are much higher compared to bone tissue or titanium alloys;

- **Ti-6Al-4V (Grade 5), Ti6Al7Nb.** Alpha/beta, near beta and beta titanium alloys are used because of their high biocompatibility coupled with good mechanical strength. Some constituent elements, such as Aluminium, are nowadays considered dangerous for the human body, but it seems that titanium alloys don’t cause severe Aluminium ion release in vivo;

- **Pure Titanium (Grade 2 & 4).** Pure titanium grades are used because of their high biocompatibility, even if their mechanical strength is strongly compromised by the absence of secondary phases. A recent, interesting use of Grade 2 Titanium is for in situ modelable components which may be adapted to the patient by the surgeon in the operating chamber.

In this thesis, the surface properties of different biomedical alloys have been studied and modified on two different levels using modern techniques in order to obtain two objectives:
**Part I: Trabecular structures for improved osteointegration of prosthetic implants.** In this part of the work, different Titanium Grade 5 and Titanium Grade 2 trabecular structures (based on larger or smaller single porosity diameter) with different morphologies have been deeply investigated in order to evaluate their suitability for their application in prosthetic implants. Morphological properties, overall porosity, mean pore diameters, and microstructure have been deeply analysed using different techniques. The mechanical properties of tensile and compressive resistance have been measured, the elastic modulus has been obtained from tensile tests and compared with literature results and biological values for trabecular and cortical bone tissue. In the last part of the work, the coefficient of friction has been evaluated against simulated and real bovine bone tissue in order to demonstrate the higher stability of the Trabecular Titanium coated prosthetic implants during surgery thanks to their morphology and bone tissue / trabecular structure localized interconnection and compenetration.

**Part II: Nanometric coatings obtained by Atomic Layer Deposition.** In this part, thin, nanometric Atomic Layer Deposition (ALD) coatings with a total thickness comprised between 10 and 280 nm, have been deeply investigated by means of Atomic Force Microscopy on the coated surface and at the interface between coated and uncoated regions, in order to determine the morphology, the defectivity and the total thickness of the ALD layers. Scanning Kelvin Probe Force Microscopy has been also used, in order to determine the electrochemical properties of the different ALD layers and to compare the effects of the different compositions. Glow Discharge Optical Emission Spectrometry has been used in order to determine both the layer thickness and the layer compositions, thanks to the capability of measuring in-depth compositional profiles, with a resolution of about 2 nm. Polarization curves have then been used in order to determine the corrosion current density and the barrier effect given by Atomic Layer Deposition for each coating configuration. Vickers indentations were also used in order to determine the delamination resistance of the coatings and for giving a fast a reliable method of comparison between different coatings. The main aim of the work was has been the evaluation of the possible use of ALD for the corrosion protection of biomedical components made of AISI 316 Stainless Steel and in particular the industrial suitability of the process. In order to propose an ALD coating suitable for industrial production, the coating thickness had to be strongly reduced (down to 10 nm) in order to reduce the deposition times and thus the overall productive costs.
INTRODUZIONE GENERALE

Nell’ambiente del corpo umano, molti materiali avanzati e leghe metalliche non possono essere attualmente utilizzati a causa della loro composizione, della loro resistenza chimica o delle loro proprietà meccaniche. È infatti ben noto che un gran numero di elementi chimici, e in particolare Antimonia, Arsenico, Bario, Berillio, Cadmio, Cromo esavalente, Piombo, Mercurio, Osmio, Tallio e Vanadio sono considerati tossici per il corpo umano e quindi la loro presenza negli impianti protesici e/o nei componenti a contatto temporaneo deve essere evitata. Altri elementi, come il Nickel, possono essere responsabili di risposte infiammatorie in pazienti sensibili o allergici. L’Alluminio non ha ruolo biologico e la sua classificazione tra i metalli tossici è controversa. Effetti tossici e accumulo sono stati infatti osservati in pazienti con problemi renali. Comunque, individui con reni sani possono essere esposti a grandi quantità di alluminio senza conseguenze. Recentemente, la sindrome di Haltzaimer è stata correlata con elevate percentuali di Alluminio depositate nel cervello. La maggior parte degli altri elementi possono avere effetti tossici quando la loro concentrazione supera alcuni valori, elementi come Ferro, Zinco, Rame e Fluoro. Per questa ragione, solo una limitata gamma di materiali può essere attualmente utilizzata per la produzione di componenti biomedici.

Le principali leghe metalliche usate in campo biomedicale sono:

- **Acciai inossidabili AISI 316L and 316LVM.** Per via della loro eccellente resistenza alla corrosione accoppiata a buone proprietà meccaniche, il 316 è largamente utilizzato per impianti chirurgici (sia temporanei che permanenti) e strumentari, dispositivi medici ed equipaggiamenti;

- **Acciaio inossidabile AISI 630.** Un buon composto tra resistenza meccanica e a corrosione, l’AISI 630 è usato spesso per strumentari e equipaggiamenti per contatto temporaneo;

- **Acciaio inossidabile AISI 420.** Grazie alla sua buona resistenza meccanica e alla mediocre resistenza a corrosione, l’AISI 420 è usato spesso per lame chirurgiche;

- **CoCrWNi (F90), CoNiCrMo (F562).** Leghe di cobalto usate per la loro resistenza ad usura e l’elevata resistenza a corrosione, anche se la loro densità e il loro modulo di Young sono molto più alti rispetto al tessuto osseo e alle leghe di titanio;

- **Ti-6Al-4V (Grade 5), Ti6Al7Nb.** Leghe di titanio alpha/beta, quasi-beta e beta sono usate per la loro alta biocompatibilità accoppiata con buone proprietà meccaniche. Alcuni elementi costituenti, come l’alluminio, sono considerati potenzialmente pericolosi per l’uomo, ma le leghe di titanio non causano forti rilasci di ioni pericolosi nell’organismo;

- **Pure Titanium (Grade 2 & 4).** Gradi di titanio puro, usati per la loro elevata biocompatibilità anche se la loro resistenza meccanica è fortemente compromessa dall’assenza di fasi secondarie. Un recente uso di interesse per il titanio Grado 2 è per componenti modellabili in-situ che possono essere facilmente adattati al paziente dal chirurgo durante l’operazione.
In questa tesi, le proprietà superficiali di differenti leghe biomedicali sono state studiate e 
modificate su due scale differenti utilizzando moderne tecnologie, con l’intenzione di 
raggiungere due obiettivi:

**Parte I: Strutture trabecolari per migliorare l’osteointegrazione degli impianti prostetici.** In 
questa parte del lavoro, strutture trabecolari a differente diametro delle porosità, realizzate in 
Titanio Grado 2 e Titanio Grado 5 e con morfologie differenti, sono state caratterizzate 
completamente per valutarne l’applicabilità negli impianti protesici. Utilizzando diverse tecniche 
si sono valutate le proprietà morfologiche, la porosità, il diametro medio dei pori. Sono state 
misurate le proprietà meccaniche di resistenza a trazione e compressione e il modulo elastico, 
confrontato poi con i valori di letteratura per l’osso trabecolare e corticale. Nell’ultima fase del 
lavoro è stato inoltre misurato il coefficiente di attrito contro tessuto osseo bovino e simulato 
per dimostrare la elevate stabilità degli impianti protesici rivestiti con le strutture trabecolari 
durante le operazioni chirurgiche, grazie alla loro morfologia e alla compenetrazione localizzata 
tra struttura e tessuto osseo, sotto la pressione dei carichi biologici e del precarico esercitato in 
fase chirurgica.

**Parte II: Coating nanometrici ottenuti per Atomic Layer Deposition.** In questa parte, 
rivestimenti nanometrici con spessore totale tra i 10 e i 280 nm sono stati applicati attraverso 
Atomic Layer Deposition (ALD) e studiati tramite Microscopia a Forza Atomica, sulla superficie e 
all’interfaccia tra zone rivestite e non, per determinare la morfologia, la difettosità e lo spessore 
totale. È stata inoltre utilizzata la tecnica Scanning Kelvin Probe Force Microscopy per 
determinare le proprietà elettrochimiche dei differenti strati ALD e confrontare gli effetti delle 
differenti composizioni. La tecnica Glow Discharge Optical Emission Spectrometry è stata inoltre 
utilizzata sia per determinare lo spessore che la composizione degli strati, grazie alla possibilità 
di ottenere profili di composizione con una risoluzione di 2 nm. Sono state effettuate Curve di 
Polarizzazione per determinare la densità di corrente di corrosione e l’effetto barriera dato dai 
rivestimenti ALD per ciascuna differente configurazione. Sono state usate inoltre indentazioni 
Vickers per determinare la resistenza alla delaminazione dei rivestimenti e per fornire un 
metodo veloce e affidabile per confrontare I diversi rivestimenti. L’obiettivo principale del lavoro 
è stato valutare la possibilità di utilizzare coating ALD per aumentare la resistenza a corrosione 
dei componenti biomedicali in acciaio AISI 316 L e in particolare valutare la possibile 
industrializzazione del processo. Allo scopo di fornire rivestimenti ALD adatti alla produzione 
industriale, lo spessore dei rivestimenti è stato fortemente ridotto (fino a 10 nm) per ridurre I 
tempi di deposizione e quindi i costi di produzione relativi.
PART I:
TRABECULAR STRUCTURES
FOR IMPROVED
OSTEOINTEGRATION OF
PROSTHETIC IMPLANTS
1- INTRODUCTION

After more than a century of continuous improvements and fast rate evolution in the orthopaedic biomaterials field, human body complexity still challenges engineers and physicians in order to obtain implants with both great biological compatibility and high mechanical characteristics.

Implant fixation enhanced by porous structures is still under intensive study, after more than 30 years of development [1]. The main problem to overcome is the necessity to balance different properties: average mechanical strength to resist to the applied load, a relatively low Young’s modulus to prevent stress shielding phenomena [2], controlled single pore dimensions to stimulate both mineral and collagen osteointegration [3], an overall porosity to grant interconnection between different pores [4], corrosion resistance under stress conditions [5] and good biocompatibility [6].

OSTHEOINTEGRATIVE TECHNOLOGIES

Different technologies are actually used in order to obtain porous metals for orthopaedic applications. The most promising and interesting ones are briefly resumed in the following paragraphs, with their main characteristics:

SINTERING

![Figure 1: Example of sintered structure: Stiktite](image1)

![Figure 2: Example of sintered structure: Sulmesh](image2)
Porous structures obtained by sintering processes can be based on titanium beads, powders (Stiktite, Smith and Nephew, Memphis, Tennessee, Fig. 1) or wires (Sulmesh, Centerpulse Orthopaedics Ltd, Winterthur, Switzerland, Fig. 2). During sintering, particles are heated below their melting temperature until they adhere with each other or to the substrate on which they are applied. Some improperly called “sintering processes” are also obtained by partial melting of the particle, for example using local welding techniques.

**PLASMA SPRAY**

![Figure 3: Example of Plasma Spray Structure: Regenerex](image)

Plasma spray is one of the most important thermal spray processes. In plasma spray the material to be deposited, typically as a powder, is introduced into the plasma jet emanating from a plasma torch. In the jet, where the temperature is on the order of 10,000 K, the material is melted and propelled towards a substrate. Using titanium powders and controlling the deposition parameters, it is possible to obtain controlled porous structures (Regenerex, Biomet, Warsaw, Indiana, Fig. 3).

**LASER / ELECTRON BEAM MELTING**

![Figure 4: Example of Electron Beam Melting: Trabecular Titanium](image)
Energy beam processes are additive manufacturing techniques in which a high energetic focused beam is used to locally melt metallic powders layer per layer, obtaining the final tri-dimensional shape. These techniques are quite flexible and the final shape of the component has almost no limitations. The main techniques actually used for biomaterials are laser and electron beam melting (Trabecular Titanium, Lima Lto, Villanova di San Daniele, Italy, Fig. 4).
**CHEMICAL VAPOUR DEPOSITION**

In a typical Chemical Vapour Deposition (CVD) process, the desired substrate is exposed to one or more volatile precursors, which react and/or to produce the desired deposit. Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber. Using precursors such as tantalum chloride and porous substrates, such as vitreous carbon foams (Trabecular Metal, Zimmer, Warsaw, Indiana, Fig. 5), it is possible to obtain porous metallic components.

**LOW TEMPERATURE ARC VAPOUR DEPOSITION**

Arc Vapour Deposition is a Physical Vapour Deposition (PVD) technique based on the formation of an electrical arc between the metallic cathodes and the anodic component that needs to be coated. The Low-Temperature Arc Vapour Deposition (LTAVD®) is an alternative techniques that operates at room temperature, making it possible to use it on a substrate with a low melting
point, such as plastic. By using different combinations of gases and metals, a variety of coatings can be deposited. Porous structures were obtained for example using titanium on polyurethane foam shells (Tritanium, Stryker, Mahwah, New Jersey, Fig. 6).

Lost wax casting is an ancient technique known since Roman times and historically used mainly on bronze. Lost-wax technique is still frequently used to manufacture small components with complex shapes in different metal alloys. In this technique, a model is used to obtain a mould with the desired shape. Wax is then cast into the mould obtaining a wax model. The wax model is then shell coated with refractory ceramic. Molten metal is then cast into the shell, melting and removing the wax. The brittle shell is then removed in order to obtain the final product. Using small trabecular wax components glued to the surface of a bulk wax model is then possible to obtain porous metallic structures (Metal Spongiosa, Eska Implants, Lubeck, Germany, Fig. 7).
MECHANICAL PROPERTIES, YOUNG’S MODULUS AND STRESS SHIELDING PHENOMENA

It is well known from literature that a correct value of Young’s modulus is required to prevent bone shielding effect. If bone is shielded and/or insufficiently loaded, bone resorption may occur. For this reason, porous structures must have moduli close to bone 10-30 GPa [7]. Bulk metallic materials are inadequate because they have much higher moduli, around 110 GPa for Ti and 230 GPa for Co-Cr alloys. This is also close to reality for coated bulk materials and single layer sintered beads/wires, as stated by Brett Levine [8] in his work. He also found the moduli values of different commercial porous structures, demonstrating that trabecular structures usually have much lower Young modulus respect to sintered and sprayed structures, comparable to cortical ones or even the spongy bone values (near 1 GPa). This is due to the elevate porosity of these structures. Similar results were also recently obtained [9] for commercial EBM porous structures (Trabecular Titanium).

Porosity is important as it influences Young’s modulus and mechanical strength. A good fitting of porosity/strength ratio is fundamental in order to obtain a porous structure applicable in orthopaedic field. Porosity obtained by sintering processes has usually quite low values if compared with other technologies. This is due to limitations in the shape and spatial arrangement of sintered particles. A partial solution is obtained using space holder particles which may be subsequently removed during or even after sintering [10]. Foam-based materials, such as CVD on vitreous carbon or LTAVD on polyurethane give the possibility to control porosity with minor changes in the substrate materials or the deposition time. Both solutions affect the diameter of the single pores and must be correctly balanced in order to obtain osteo-integrative properties. Plasma spray coatings, being influenced by thermal/flow dynamic parameters, mean powder dimension and powder diameter distribution, cannot give an easy and complete control of porosity and require specific calibrations for each process. Nevertheless, high porosity values were presented in different literature papers [11-12]. Local melting techniques, such as Electron Beam and Laser Beam Melting, offer a theoretical easier control on porosity, since they only depend on the CAD 3D models they are based upon, which can be easily modified by the operator. In the practice, this is often limited by the dimension of the powder and the radius of the beam itself. The range of different structures obtained in literature with these technologies [13-14] suggest that this partial limitation can be easily solved.

Figure 8: Absence of interface between bulk component and Trabecular Titanium
Interface bonding is also fundamental for implant stability. Using laser, Electron Beam Melting (Fig. 8) or lost-wax casting, the presence of an interface between bulk and porous structure is definitely avoided. Technologies which involve partial melting (sintering), if optimized, can show a similar behaviour. For all the other processes, mechanical or high-temperature treatments are required in order to obtain strong binding forces between the two different components (Fig. 9).

Stress concentration is also typical in these structures, due to the presence of porosity and the strong reduction of resistant area, as shown by Manley et al. [15]. The long term behaviour of porous structure cannot be easily predicted, and this is even more evident in structures with random disposition, such as plasma spray, as the shape and dimensions of single porosities follow a statistical distribution. This effect is less evident in ordered structures such as EBM, Sintered Wires, Lost-Wax Casting and partially CVD on vitreous carbon.

Surface micro-roughness is critical in triggering fatigue cracks, as it is the distribution of defects [16]. Most porous structures for biological application have in fact really high surface micro-roughness that may have effect in compromising the fatigue life of the component.
Tissue response and osteo-integration

In his work, Turner [3] states that the minimum pore size needed to ensure that mineralized bone is regenerated is of the order of 100 µm, while pores with less than 10 µm have been shown to inhibit the in-growth of cells, pore sizes of 10-75 µm encourage fibrovascular in-growth and pore sizes of 75-100 µm result in in-growth of unmineralized osteoid tissue. This is related to the dimensions of the harvesian systems, that usually have an average diameter of 100-200 µm. Frosh et al. [17] concluded that the growth of human osteoblasts in drill channels, having a diameter of 600 µm, was significantly quicker than in all other channels with diameters ranging from 300, 400, 500, and 1000 µm, as it is common knowledge that a fast osteointegration is important in order to obtain optimal fixation of the component and prevent mechanical failures and detachments. These two different works give a clear idea of the wide optimal range of diameters for open porosities in orthopaedic materials.

Techniques like lost-wax casting can hardly reach these low values. In sintering processes, the single porosity diameter is mainly related to the dimension of the sintered objects themselves and for this reason small, for example, in the case of sintered powders. For both CVD and LTAVD processes pore diameter may be fitted changing the morphology of the foam substrate or changing the deposition time, in order to achieve the desired values. Laser or Electron Beam Melting permit to obtain new structures simply changing their CAD 3D model. This can also be achieved, with a greater time effort, with a precise optimization of the beam diameter and energy.

The ideal osteointegration of a component vary as a function of the application, since components with low loads don’t usually need deep osteointegration, while some components are not always lifelong lasting (acetabular cups, for instance) and may need revision. Implants that may require revision have to be removed relatively easily from bone, in order to limitate the damage to human body tissues.
Corrosion and biocompatibility

Few metallic alloys are actually used in orthopaedic porous structures, the four most important being Titanium CP Grade 2, Tantalum, Titanium Ti-6Al-4V Grade 5 and Co-Cr alloys. This is mainly because of their high corrosion resistance and biocompatibility. For metallic alloys, these two aspects are strictly connected. The great importance of corrosion resistance is mainly related to two aspects: ion-release occurring during electrochemical reactions and mechanical failures triggered by corrosion phenomena. Most metallic alloys contain elements that may be dangerous if released into the human body, so electrochemical reactions and ion dispersions from the component must be limited. Corrosive phenomena may also form small defects on the surface of the component, such as pitting. These small defects may trigger failures, reducing mechanical strength in particular under fatigue conditions.

Due to their peculiar morphology, porous structures have great area / volume ratios, showing higher corrosion rates compared to conventional non porous-coated implants [18]. Galvanic coupling between porous structure and bulk component may also be present if the composition of the two alloys is different, further enhancing corrosion rate [19]. CP titanium and Tantalum exhibit the best biocompatibility and corrosion resistance, but usually lack in mechanical strength. For this reason, they are usually coupled with other materials in the orthopaedic field.

Bundy et al. [18] investigated stress-enhanced ion release (SEIR) of polished, grit-blasted and porous coated surfaces, finding that stress affected a number of corrosion parameters, lowering the breakdown potentials and increasing corrosion currents. This can became a problem, in particular for Grade 5 Titanium and Co-Cr alloys [19][21]. As stated by Ryan et al. [7] more biocompatible materials cannot be used actually for these applications due to their intrinsic brittleness (ceramics) or their incapability of sustaining the mechanical forces present in joint replacement surgery (polymers).
Clinical application

Figure 10: Radiography of Stiktite prosthetic hip implant

Figure 11: Radiography of Sulmesh prosthetic hip implant

Figure 12: Radiography of Regenerex prosthetic hip implant

Porous metallic structures already found orthopaedic applications in different components in which osteointegrative processes are necessary to grant implant stability, such as acetabular cups, stems, and cervical devices. Clinical data, such as the post-implant radiography of acetabular cups presented for all the technologies in figures 10 to 16, clearly show that all the
investigated techniques may grant optimal osteointegration with time. Clinical results were published for some of the technologies listed before. Sintered wires (Sulmesh) coated acetabular cup, for example, showed a 100% survival rate on 100 analyzed acetabular cups after a follow-up time of 9.7 years [23], where revision was considered the end-point. CVD of tantalum on vitreous carbon (Trabecular Metal) showed a 98.3% survival rate in similar conditions on 60 analyzed acetabular cups and a follow-up time of 14-68 months [24] and a similar survival rate for 105 Total Knee Arthroplasty with a follow-up time of 36-56 months [25]. Lost-wax casting (Metal Spongiosa) showed an 88.8% survival rate in 15-17 years on 165 analyzed acetabular cups, with variable degree of stress shielding phenomena in 21% of cases [26]. Plasma spray technique clinical results showed a 94% survival rate with a follow-up time of 76 months in 177 femoral components using Mallory-Head Porous femoral component (Regenerex) [27]. In all cases, good osteointegration of the implant was observed and revisions mainly occurred due to fracture secondary to trauma, component undersizing and infections. Really few revisions were due to component failure. No clinical results can be found nowadays in literature for EBM titanium, titanium powder sintering and LTAVD, even if preliminary data on canine hip models and intramedullary

![Figure 13: Radiography of Trabecular Titanium Prosthetic Hip Implant](image13)

![Figure 14: Radiography of Trabecular Metal Prosthetic Hip Implant](image14)

rabbit rods results showed promising bone ingrowth for LTAVD (Tritanium) [28].
Implant clinical data and preliminary results actually in literature seem to be promising for reliable lifelasting biocompatible implants, but long-term data and a wide statistical investigation are fundamental in order to evaluate the real characteristics of osteointegration granted by the different techniques. For this reason, a complete and reliable comparison of all techniques will only be possible in the future.

**Figure 15:** radiography of Tritanium prosthetic hip implant

**Figure 16:** radiography of Metal Spongiosa prosthetic hip implant

**References**


[18] L. Reclaru, P.Y. Eschler, R. Lerf, A. Blatter, Electrochemical corrosion and metal ion release from Co-Cr-Mo prosthesis with titanium plasma spray coating, Biomaterials, 2005; 26, 4747-56;


2- Introduction to Electron Beam Melting Technology

Electron beam melting (EBM) is a type of additive manufacturing for metal parts. It is often classified as a rapid manufacturing method, even if EBM is actually used in a wide range of productive industrial applications, in particular in the biomedical field for osteointegrative prosthetic implants. The technology manufactures parts by melting metal powder layer per layer with an electron beam in a high vacuum. Unlike some metal sintering techniques, the parts are fully dense, void-free, and can show high mechanical performances comparable with similar components obtained with conventional productive methods.

EBM industrial interest, in particular, is concentrated on the possibility to produce components with geometrical shapes not compatible with standard productive methods, hollow, trabecular or extremely complex.

Melting obtained by electron beam

Figure 17 shows a simple scheme of a typical EBM chamber. This solid freeform fabrication method produces fully dense metal parts directly from metal powder with the same chemical composition of the target material. The EBM machine reads data from a 3D CAD model and lays down successive layers of powdered material. Powder excesses are then removed by a leveling blade which also levels the powder in order to obtain an homogeneous working surface. These layers are successively melted together utilizing a computer controlled electron beam. In this way the EBM equipment is able to produce tri-dimensional components. The process takes place...
under vacuum, which makes it suited to manufacture parts in reactive materials with a high affinity for oxygen, e.g. titanium.

The melted material is from a pure alloy in powder form of the final material to be fabricated, without the use of a filler material, which is usually necessary during layer by layer rapid manufacturing due to the relatively low energy of the heat source. For that reason the electron beam technology doesn't require additional thermal treatment to obtain the full mechanical properties of the parts.

That aspect allows classification of EBM with selective laser melting (SLM) as a complete manufacturing technique, where competing technologies like Selective Laser Sintering (SLS) and Direct Metal Laser Sintering (DMLS) require thermal treatment after fabrication. Comparatively to SLM and DMLS, EBM has a generally superior build rate because of its higher energy density and scanning method.

The EBM process operates at an elevated temperature, typically between 700 and 1,000 °C, but up to 2000 °C for melting processes involving titanium or cobalt alloys, even if the Electron Beam itself may reach the temperature of 15000 °C due to the high kinetic energy of the electrons (Figure 18).

The typical melt rate for a modern EBM process is up to 80 cm³/h, with a minimum layer thickness of about 0.05 millimeters (0.0020 in) and a tolerance capability: +/- 0.2 mm, even if these values are also dependent on the chemical and physical characteristics of the melt alloy. Parameters such as surface tension, thermal conductivity, specific heat, may in fact have an influence on the tolerance values for the final component.

**Figure 18: Photograph of an electron beam and a melted metal pool**
EBM Industrial Applications

Industrial applications of EBM (Figure 19) are strongly limited due to the high costs related to the EBM techniques, the low load capabilities of the modern EBM chambers and the high amount of time required for the process due to the necessity to work under vacuum conditions and with only one heat source that, during melting, has to scan over the whole surface.

For these reasons, EBM is nowadays considered convenient only for the production of customized components or components of high final value, such as biomedical prosthetic implants.

Some industrial applications of EBM are listed below:

- Biomedical: Implants with engineered porosity and cellular surface structure to facilitate bone ingrowth, batch series production of standard and special orthopaedic implants, production of custom design implants;
- Aerospace: production of gas turbine engine compressors parts (in particular support cases), small aerospace prototypes, rocket engine impellers and landing gear components;
- Industrial: production of racecar light structural components, such as uprights, gearbox casings, engine parts with lattice porous structure, production of small pressurized heat exchangers.
Chapter 2: Introduction to Electron Beam Melting Technology
3- CHARACTERIZATION OF TRABECULAR TITANIUM

DESCRIPTION OF SAMPLES

Trabecular Titanium™ is a Trademark trabecular structure produced by LimaCorporate using Electron Beam Melting processes.

In the first phase of the process, a tri-dimensional structure has been built using a CAD3d program. The basic element of the CAD 3d matrix is a hexagon developed on three planes. The matrix built on this element is then cut using boolean operators on planes and curves to obtain the desired shape (Fig. 20).

Three different sample structures were tested in this project:

- **Structure A**: smaller, with pore dimension comparable to Trabecular Metal and adequate for the fast ingrowth of singular harvesian systems (about 250 µm diameter);
- **Structure B**: with pore dimension comparable to literature results for the fastest osteointegration of prosthetic implants (about 650 µm diameter);
- **Structure C**: with larger pore dimension (about 1400 µm diameter), over the maximum values for a fast osteointegration, but with a lower elastic modulus, closer to trabecular human bone;

The name of all of these structures is Trabecular Titanium™ [1]. Trabecular Titanium™ (TT) specimens were provided by manufacturer Lima-Lto Medical Systems (Villanova San Daniele del Friuli, Italy).

For the characterization, two different titanium alloys were employed:
• **Ti-6Al-4V (Grade 5):** Titanium alloy with high corrosion resistance and biocompatibility coupled with superior mechanical characteristics due to its α-β structure;

• **Pure Titanium (Grade 2):** Commercially pure Titanium with superior biocompatibility and lower mechanical modulus, coupled with lower mechanical characteristics due to its pure α structure.

For the characterization, 10.5 mm diameter x 12 mm height cylinders have been modelled to be used for both microstructural characterization and for compression stress test. Dog-bone shaped flat samples (5.5 x 3 mm, 100 mm length with 11 x 3 mm ends) were prepared for tensile strength test and 25.4 mm diameter samples were also produced for adhesion test, using a sandwich structure made of a 2 mm cellular layer in between the two layers of bulk material.

Some 10.5 mm cylindrical samples (not used for compression strength tests) were cut and embedded in phenolic resin then polished in order to reach a surface roughness under 0.1 μm Ra. These samples were then observed using optical and electronic microscopy. Some other samples were used for porosity measurements using three different methods: Archimedes principle's method, calibre and scale method and, filling the porosity with water and observing the change in weight.
Characterization

Titanium powders were obtained from a commercial supplier. Powders were observed by Scanning Electron Microscope (SEM, EVO-40 Carl Zeiss) and analysed using Energy-Dispersive X-ray Spectroscopy (EDXS) and Laser Diffraction Granulometry (LA-950 Horiba Scientific), in order to obtain information about their morphology, chemical composition and dimensions distribution.

For density tests a standard Archimedes principle's kit has been used. For relative density the kit has been slightly modified adding a Parafilm shell to isolate the cellular solid's porosities from water. Knowing the weight in air of sample \( W_s \) and Parafilm \( W_p \), the sum of them \( W_{ps} \) the density of Parafilm \( \rho_p \) and Ti6Al4V \( \rho_{Ti} \) and knowing the weight of the composite Parafilm + sample + air in water \( W_{ps}^w \) defining \( \rho_s \) it is possible to obtain the density of the sample and its relative density \( \rho_r \), simplifying the weight of the air in water:

\[
\rho_r = \frac{\rho_s}{\rho_{Ti}} = \frac{W_s}{V_s} = \frac{W_s}{(V_{ps} - V_p)\rho_{Ti}} = \frac{W_{ps}^w}{(W_{ps} - W_{ps}^w - V_p\rho_p)\rho_{Ti}}
\]

Density of Parafilm \( (0.77\pm0.01 \text{ g/cm}^3) \) was given by producer (American National Can™) and verified using scale and calliper on rectangular samples. Volume of Parafilm has been obtained using a calliper on a regular shaped sample of material.

Another relative density test has been made using an adherent latex shell fixed on the sample and filling it up with a syringe of water. Calculating the weight of the sample and the latex \( W_{sl} \) and the weight of the sample and latex plus the water \( W_{sl}^w \) it was thus easily possible to obtain the relative density:

\[
\rho_r = \frac{\rho_s}{\rho_{Ti}} = \frac{W_s}{\rho_{Ti}(V_s + V_w)} = \frac{V_s}{V_s + V_w} = \frac{W_s}{W_s^w + V_w\rho_{Ti}} = \frac{W_s}{W_s^w + V_w\rho_{Ti}}
\]

The last method used to calculate relative density was obtained simply by using a calibre and a balance:

\[
\rho_r = \frac{W_s}{\pi r^2 h}
\]

The results of the three different methods were then compared and average values were obtained.

An evaluation of the dimensions of the porosity was performed using image post processor software for microscopes. The main problem in porosity dimension measurement was its relativity. As the porosity of a cellular solid is a function of spatial position and cutting plane, the porosities were measured on each single uncut element of the structure. This porosity evaluation method is totally new and only applicable in regular 3D solids. Considering one
hexagonal element, the porosity is the projection of the 3D porosity of the element on a plane passing only for two opposite vertices and the centre of gravity of the element. This value was obtained by observing the sample from one side and knowing the angles that the element forms in relation to the sample.

Vickers micro-hardness $HV_{0.1}$ (0.981 N) was obtained on the cellular solid structure using a few expedients. Metal arm thickness in a polished sample is not certain, therefore micro-hardness measures are strongly influenced by the hardness of the resin around the sample. The use of transparent resin gave a better, but still not perfect, knowledge of the thickness of metal arms. Micro-hardness measures were considered good only if at least 200 µm far away from metal edges and at least 500 µm away from another micro-hardness indentation vertex.

Alloy chemical analyses was obtained using Energy-Dispersive X-ray Spectroscopy (EDXS). This method gives a semi-quantitative analyses, affected by an error that can be as great as 6% in weight, and much more for Carbon [2]. This analysis was used to roughly evaluate the bulk metal composition after sintering and, in combination with Backscatter Imaging, to search for defects and inclusions.

Compression, tension and adhesion tests were made by Lima-Lto laboratories using UMTS model (Insight 100), and fracture analyses were carried out using SEM to detect the trigger point and observe the morphology of fracture surfaces and necking on the metal arms of the cellular solid's structure.

The “adhesion test” is a particular medical required tension test on a 25.4 mm diameter sample aimed to evaluate adhesion of a coating applied on a substrate. To validate components made by EBM technology this kind of test must be performed even if a coating is not present. For this purpose samples were prepared as follows: a 25.4 mm diameter sandwich structure made of dense-porous-dense material with a 2 mm thick porous layer using EBM (Fig. 21). To pass the test, the fracture of the sample must occur in the porous structure and not at the interface between porous and dense material.

**Figure 21: CAD3D Model of a Tensile Sample to Measure Adhesion**
All sample dimensions for tension and compression tests were strongly limited by the necessity of Lima-Lto to compare the results with other porous materials which were previously investigated. For this reason, the scattering in the mechanical properties results is usually high.
References


4 - Test Results

Powder Analysis

Powder chemical composition was analysed by the producer obtaining the results in Table 5, confronted with the standard composition of the same alloys:

<table>
<thead>
<tr>
<th></th>
<th>Ti</th>
<th>Al</th>
<th>V</th>
<th>O</th>
<th>Fe</th>
<th>N</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade 5 Powder</td>
<td>Bal.</td>
<td>5.78%</td>
<td>4.13%</td>
<td>0.08%</td>
<td>0.15%</td>
<td>0.005%</td>
<td>0.009%</td>
</tr>
<tr>
<td>Grade 5 Standard</td>
<td>Bal.</td>
<td>6%</td>
<td>4%</td>
<td>&lt;0.10%</td>
<td>&lt;0.25%</td>
<td>&lt;0.01%</td>
<td>&lt;0.03%</td>
</tr>
<tr>
<td>Grade 2 Powder</td>
<td>Bal.</td>
<td>-</td>
<td>-</td>
<td>0.12%</td>
<td>0.05%</td>
<td>0.024%</td>
<td>0.006%</td>
</tr>
<tr>
<td>Grade 2 Standard</td>
<td>Bal.</td>
<td>-</td>
<td>-</td>
<td>&lt;0.25%</td>
<td>&lt;0.3%</td>
<td>&lt;0.03%</td>
<td>&lt;0.1%</td>
</tr>
</tbody>
</table>

Powder morphology was investigated using SEM (Fig. 22). Most of the powder particles show a near-spherical shape, which is typical for atomization processes. The particle diameters range between about 10 and 100 microns, with a statistical mode between 50 and 60 microns.

Figure 22: Titanium powders as observed by SEM
The statistical distribution of the particle dimensions is presented in Fig. 23 in logarithmic scale. The mean value is close to 60 µm, with a really narrow distribution. Almost no particles were found to be under 40 or over 80 µm. More than 50% of the particles were found to be in the range between 50 and 60 microns.

**Figure 23: Powder distribution**
STRUCTURE MORPHOLOGY

Fig. 24 shows the structure of sample (A) as obtained with the EBM process and Ti6Al4V alloy powders, followed by blasting, to remove any residual metallic not melted powder. The metallic surfaces appear pleated and irregular, the single porosity does not appear as a hexagon but as an irregular shape. Single porosities show comparable dimensions. All corners and vertices appear rounded off, and the single metallic arm (metallic conjunction between two contiguous nodes of the structure) has an approximate diameter of 250 μm, comparable with the diameter of the singular porosities.

Fig. 25: CAD3d model of trabecular titanium (structure B)

The complex, irregular structure obtained with the EBM process, totally different from the CAD3d version (Figure 25), cannot be easily simulated using 3d software, therefore EBM 3d porous structures need a complete characterization every time a process parameter is changed.
Figure 26 shows the structure of sample (B) as obtained with the EBM process and Ti6Al4V alloy powders, followed by blasting, to remove any residual metallic not melted powder. The metallic surfaces appear pleated and irregular, the single porosity does not appear as a hexagon but as an irregular, almost round shape. Single porosities show comparable dimensions. All corners and vertices appear rounded off, and the single metallic arm (metallic conjunction between two contiguous nodes of the structure) has an approximate diameter of 700 μm, comparable with the diameter of the singular porosities.

Figure 26: Trabecular Titanium Structure B

Figure 27 shows the structure of sample (C) as obtained with the EBM process and Ti6Al4V alloy powders, followed by blasting, to remove any residual metallic not melted powder. The metallic surfaces appear pleated and irregular, the single porosity does not appear as a hexagon but as an irregular, almost round shape. Single porosities show comparable dimensions. All corners and vertices appear rounded off, and the single metallic arm (metallic conjunction between two contiguous nodes of the structure) has an approximate diameter of 700 μm, almost double respect to the diameter of the singular porosities.
Figure 27: Trabecular Titanium Structure C
Fig. 28 shows the output of the image post-processing used to measure the dimension of the structural voids. The results are shown in Tab. 2.

The results of the structural voids dimension test were reliable for all samples, usually not differing more than 5% from the average value. As expected, sample B shows bigger porosities and a greater dispersion in the results. According to literature, due to pore dimensions and percent of porosities, trabecular sample A is expected to allow a well balanced and fast osteointegration.

**Table 2: Areas and diameters of the porosities of the different structures**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Area</th>
<th>Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mm²</td>
<td>mm</td>
</tr>
<tr>
<td>Structure A</td>
<td>0.11 ± 0.05</td>
<td>0.28 ± 0.07</td>
</tr>
<tr>
<td>Structure B</td>
<td>0.34 ± 0.11</td>
<td>0.66 ± 0.09</td>
</tr>
<tr>
<td>Structure C</td>
<td>1.48 ± 0.19</td>
<td>1.37 ± 0.15</td>
</tr>
</tbody>
</table>
Part I
Chapter 4: Test Results

**Relative Density**

The relative density was measured following three different procedures, as described in the experimental details. The results are reported in Table 3 as percentage of porosity for all three different samples:

**Table 3: Density results for the different structures**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Calibre</th>
<th>Parafilm</th>
<th>Latex Shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure A</td>
<td>54.32 ± 0.27</td>
<td>53.29 ± 0.19</td>
<td>49.55 ± 1.15</td>
</tr>
<tr>
<td>Structure B</td>
<td>64.55 ± 0.35</td>
<td>62.31 ± 0.16</td>
<td>61.13 ± 0.75</td>
</tr>
<tr>
<td>Structure C</td>
<td>84.34 ± 0.41</td>
<td>-</td>
<td>85.86 ± 1.21</td>
</tr>
</tbody>
</table>

Unfortunately the Parafilm test on Structure C could not be performed due to flotation of the structure in water. Other liquids with a lower density may be used for this kind of test, such as alcohol or acetone, but the high evaporability of these substances may have great influence on the results.

Since both the Grade 5 and the Grade 2 based processes were optimized in order to obtain the same porosity for both titanium alloys, the relative density tests presented in this work are only relative to Grade 5 Structures. Results obtained on Grade 5 and Grade 2 structures were in fact comparable and repeatable.

The relative density tests were performed considering the mean value of 4.43 g/cm³ as density of the Ti6Al4V alloy. All three tests were comparable and reliable, giving less than 2% of difference in the results. The data dispersion for every single method used (Caliper, Latex Shell or Parafilm) was quite low, giving 2% or less in difference between the measurements. The Caliper method proved to be faster but less accurate and strongly influenced by possible human errors. The Latex Shell method proved to be reasonably accurate but still quite influenced by human error. The Parafilm method proved to be extremely accurate but not applicable to light, highly porous structures due to floating. In the literature [2-4] different values for natural bone's porosity can be found for spongy bone (50-80%) and cortical one (5-10%). Cortical bone porosity is greatly different from the results obtained for both samples. On the other hand, it is well known that osseointegration has a greater effect if the porous material has a porosity similar to the one of spongy bone. Therefore the results obtained from both the samples produced can be considered interesting for applications that require osseointegration. In other papers Ti-6Al-4V structures obtained by EBM gave different porosity results depending on the geometry of the structure obtained during the process. EBM technology can be successfully used to obtain structures with porosity from 60 up to 95% [5] simply changing the geometrical parameters of the single cell. Other materials for osseointegration described in the literature such as those obtained by CVD (Chemical Vapour Deposition) of tantalum on vitreous carbon skeleton can give up to 80% of porosity [6-7].
**MICROHARDNESS**

Vickers micro-hardness tests (HV0.1) were performed on specific structure areas and in particular on arms and nodes, giving the results shown in Tab. 4.

**Table 4: Microhardness of the different structures and different titanium grades**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Grade 5</th>
<th></th>
<th>Grade 2</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Arms</td>
<td>Nodes</td>
<td>Arms</td>
<td>Nodes</td>
</tr>
<tr>
<td></td>
<td>HV0.1</td>
<td>HV0.1</td>
<td>HV0.1</td>
<td>HV0.1</td>
</tr>
<tr>
<td><strong>Structure A</strong></td>
<td>374.3 ± 17.9</td>
<td>376.4 ± 15.8</td>
<td>305.6 ± 55.1</td>
<td>308.4 ± 45.2</td>
</tr>
<tr>
<td><strong>Structure B</strong></td>
<td>378.4 ± 15.2</td>
<td>380.6 ± 12.1</td>
<td>309.2 ± 65.3</td>
<td>303.7 ± 48.8</td>
</tr>
<tr>
<td><strong>Structure C</strong></td>
<td>381.6 ± 13.0</td>
<td>366.2 ± 20.2</td>
<td>293.0 ± 23.0</td>
<td>299.2 ± 31.9</td>
</tr>
</tbody>
</table>

Mean nodes and arms values are almost the same for both samples (only 1% difference), suggesting that the metal has a similar microstructure in both samples. Titanium is a much harder metal than aluminium and approaches the high hardness possessed by some of the heat-treated alloy steels. Ti-6Al-4V alloy usually has a micro-hardness ranging from 160 HV to 320 HV. A mean value of approximately 380 HV suggests that the micro-structure of the sample is fine, regular and homogeneous, due to a quite fast cooling procedure of the melted titanium drops during the EBM process.
MECHANICAL CHARACTERIZATION

Mechanical characterization was then carried out performing tensile and compression tests. Tensile tests (Table 5 and Figures 29 and 30) gave the following results:

![Figure 29: Tensile test results performed on Titanium Grade 2](image1)

![Figure 30: Tensile test results performed on Titanium Grade 5](image2)
Table 5: Tensile test results for both Grades and all Structures

<table>
<thead>
<tr>
<th>Grade</th>
<th>Structure</th>
<th>Peak Load</th>
<th>Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MPa</td>
<td>%</td>
</tr>
<tr>
<td>Grade 2</td>
<td>A</td>
<td>15.8 ± 0.1</td>
<td>5.03 ± 0.44</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>13.5 ± 0.1</td>
<td>6.47 ± 0.72</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>5.3 ± 0.7</td>
<td>12.15 ± 8.25</td>
</tr>
<tr>
<td>Grade 5</td>
<td>A</td>
<td>55 ± 7.5</td>
<td>3.27 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>40 ± 12</td>
<td>4.1 ± 0.21</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>23 ± 1.5</td>
<td>3.68 ± 0.36</td>
</tr>
</tbody>
</table>

Peak stress for Samples obtained in Titanium Grade 2 was higher compared to Samples obtained in Titanium Grade 5, as expected. For all three structures, the values of Peak Load of Titanium Grade 5 are from three to four times higher, while the elongations were always higher in the case of Titanium Grade 2.

In the case of Grade 2 alloys, the stress-strain curves can be clearly divided in two different regions, one of elastic behaviour, nearly linear and relatively small, and one of plastic behaviour, where the relationship between stress and strain is not linear and the samples are in plastic deformation regime, with higher relative elongations at relatively small load increases. This behaviour can be considered typical for a Grade 2 alloy, which is composed by a singular phase and has no hardening agents such as carbides or secondary phases. Going from structure A to structure C it is possible to observe that the plastic region is wider and the samples reach longer deformations before breaking occurs. This is caused by the lower stiffness of the samples and the peculiar structure which acts as a tri-dimensional spring.

In the case of Grade 5 alloys, the stress-strain curves for Samples A and B are nearly linear, which indicate an elastic behaviour and a low plastic deformation at high loads, just before fracture. This is the typical behaviour for Grade 5 Titanium Alloys, in which the presence of the β-phase enhances the mechanical characteristics of the alloys but reduces the deformability. Sample C shows greater plastic deformation before fracture and a higher mean elongation, which can possibly be due to the lower stiffness, as already observed on the samples obtained with the Grade 2 alloy.

The result dispersion in these materials is usually high [8] as confirmed by the graphic plots. High dispersion is caused by the presence of a relatively small number of metallic arms in each section of the structure. During the tensile test some of these arms break, but the structure does not until a certain amount of arms are broken on the same 45° inclination plane (the one with the lower resistant area). When this number is exceeded the structure instantaneously breaks. If the number of arms in a section is too low (from 2 to 20) the breaking of a single arm may lead to a structure breaking because of the sensible variation of the resistant area.

Compression tests (Table 6 and Figures 31 and 32) gave the following results:
Figure 31: Compressive test results performed on Titanium Grade 2

Figure 32: Compressive test results performed on Titanium Grade 5
TABLE 6: COMRESSIVE TEST RESULTS FOR BOTH GRADES AND ALL STRUCTURES

<table>
<thead>
<tr>
<th>Grade</th>
<th>Structure</th>
<th>Peak Load</th>
<th>Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MPa</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>16.2 ± 2</td>
<td>4.04 ± 0.31</td>
</tr>
<tr>
<td>Grade 2</td>
<td>B</td>
<td>13.4 ± 1</td>
<td>6.03 ± 0.24</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grade 5</td>
<td>A</td>
<td>74 ± 3</td>
<td>8.38 ± 0.51</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>60 ± 4</td>
<td>10.75 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>26 ± 1</td>
<td>11.98 ± 0.59</td>
</tr>
</tbody>
</table>

Compressive tests were not obtained for Grade 2 Structure C due to the extremely low mechanical resistance of the cylindrical samples which broke apart during the approaching procedures of the testing apparatus.

Peak stress for Samples obtained in Titanium Grade 2 was higher compared to Samples obtained in Titanium Grade 5, as expected. For all three structures, the values of Peak Load of Titanium Grade 5 are more than four times higher, while the elongations were always higher in the case of Titanium Grade 2.

In the case of Grade 2, the stress-strain graph shows two areas for both Structure A and Structure B. In the beginning, the samples have an elastic behaviour until deformation reaches about 0.5 mm. This may be compared to the action of a spring being compressed. This region of the graph is then followed by a fast collapse of the structure, which becomes come compact without requiring an increase of applied load. After the collapse, the stress-strain graph shows a new increase before the breakage.

In the case of Grade 5, the stress-strain graph shows different areas, for all Structures. In the beginning, the samples have an elastic behaviour until deformation reaches about 0.5 mm. This may be compared to the action of a spring being compressed. In a second moment, the graphs shows a plastic deformation of the sample. In a third moment, the structure collapses, illustrating a minor stress requirement in order to maintain constant the strain over time. This is due to the bending of the metallic arms over a critical “no return” angle. Structure C samples break in this part due to its actual lower resistant area. Afterwards, the structures A and B compact into an almost full cylindrical sample. Before the break, the graphs show a new increase in the stress, which is due to the sample acting as bulk material. This part is particularly limited due to the previous intensive deformation which compromised the mechanical resistance of the structure.

Peak stress for Structure A resulted to be the 25% higher than Structure B which was more than double with respect to Structure C. In this test the dispersion of data was very low as for full density metallic samples. In this case, the difference between Structure B and Structure C is caused by the high deformation that structure C requires before compacting enough to act as a compact component.

In literature, extremely porous structures proved to have very low compressive strength [5-6]. Harrysson et al. [6], Heinl et al. [10] and Li et al. [11] obtained high compressive strength with
porosities comparable with those of Trabecular Titanium Structures B and C. The difference between these structures is mainly in the different geometrical parameters of the single cell and/or the entire structure. Li et al. [11] structure, for example, has a strong orientation that gives a higher actual resistant section in the direction chosen for the compression test. This phenomena explains the impressive results obtained. Instead, Heinl et al. [10], obtained a performing hatched structure having both a good mechanical strength and a good porosity, but with narrow single porosities and a higher density of metallic arms resulting in a more homogeneous distribution of the metallic arms in the whole volume of the sample.

Tension tests of adhesion gave the following results (Table 7):

**Table 7: Results of the tensile adhesion tests**

<table>
<thead>
<tr>
<th>Grade</th>
<th>Structure</th>
<th>Test result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade 2</td>
<td>A</td>
<td>Passed</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>Passed</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>Passed</td>
</tr>
<tr>
<td>Grade 5</td>
<td>A</td>
<td>Passed</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>Passed</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>Passed</td>
</tr>
</tbody>
</table>

In any case, the cellular layer did not detach from the bulk material but was broken apart. This is a good result for this type of analysis. The applied load used to break apart the structure is strongly influenced by the orientation of the trabecular structure, proving that the cellular solid structure is isotropic.

It is common knowledge that the basic cell of the structure can be varied by means of a particular production process depending on the application. For orthopaedic implant applications the high density low diameter porosities (i.e. smaller structure) is a well-suited structure to acquire a trabecular bone phenotype.
Influence of the Structure Orientation on Mechanical Properties

In order to be easily confronted, all the mechanical tests were performed using the same orientation for the Trabecular Structure.

Simple tensile tests were also performed to discriminate the effect of the structure orientation respect to the load direction. From the data collected, it resulted that the orientation of the applied load respect to the orientation of the trabecular structure may affect the mechanical resistance of Trabecular Titanium up to about 30% and the test results shown in the previous section were obtained from the most mechanically resistant orientation possible for the Trabecular Titanium samples.

The mechanical resistance of Trabecular Titanium respect to orientation of the structure resulted to be mainly affected by two different phenomena:

1) It was possible to observe that the Trabecular Titanium structures have a preferential structure breaking orientation, caused by an intrinsic reduction of resistant area in a particular orientation (Figure 33). This orientation resulted to be inclined about 45° with respect to the standard productive orientation of Trabecular Titanium;

![Figure 33: Preferential breaking orientation on Trabecular Titanium Structure](image)

2) The EBM melting process resulted to have a preferential Trabecular Titanium structural orientation due to its layer-by-layer nature. It was observed that more defective or less thick metallic arms were present in the case of EBM samples in which the structure was not built following the standard productive orientation (Figure 34) leading to a lower mechanical resistance of the component.
Figure 34: Defective Trabecular Titanium arm (incomplete structure due to orientation)
TRABECULAR TITANIUM FRACTURE ANALYSIS

In Figure 35, the typical site of fracture for a metallic arm of the structure is illustrated, for both Titanium Grade 5 (a) and Titanium Grade 2 (b) alloys after tensile tests. In these two examples the metallic arms has been ripped off in proximity of a node, leaving a curved cup-like fracture surface composed of cavities and division phenomena, that clearly indicates a ductile nature of both titanium alloys.

In the case of Grade 2 (b), the ductile nature of the alloy is more evident, as the morphology in the centre of the fracture is more rough, indicating a more intense plastic deformation of the material before breaking occurred.

In both Figures, some neckings on the arms’ sides can be observed, while in Figure 35a it is possible to observe the presence of a second fracture near the first one, on the left.

In Figure 36 the internal structure of a structure's fracture of Titanium Grade 5 (a) and Titanium Grade 2 (b) is shown, at high magnifications. It can be observed that the fracture microstructure is mainly composed by cavities and division surfaces. The presence of both of these characteristics is typical for ductile fractures. Both metallic arms have broken due to nucleation and growth of micro-voids formed on the grain boundary. When the void volumes (interacting
with each other) reached the critical dimension, the structure collapsed thus resulting in a ductile fracture.
Elastic Modulus

The elastic modulus of Trabecular Titanium has been measured and compared with literature results for other EBM structures made in Ti-6Al-4V. All the analysed structures show a low elasticity modulus which is easily comparable with the value of spongy bone, and strongly inferior to that for cortical bone. In particular, Trabecular Titanium C shows an elastic modulus which can be considered equal or even inferior to the value of trabecular bone. Other EBM structures show similar values, like those analyzed by Cansizoglu et al. [5] and Heinl et al. [10].

Table 8: Elastic modulus of the different Trabecular Structures

<table>
<thead>
<tr>
<th>Grade</th>
<th>Structure</th>
<th>Elastic Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bone</td>
<td>Cortical</td>
<td>~18</td>
</tr>
<tr>
<td></td>
<td>Trabecular</td>
<td>~1</td>
</tr>
<tr>
<td>Grade 2</td>
<td>A</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.6</td>
</tr>
<tr>
<td>Grade 5</td>
<td>A</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.9</td>
</tr>
</tbody>
</table>

The elastic modulus of bulk materials used in the orthopaedic field for osteointegrative components, such as Titanium, Cobalt or Stainless Steel, is more than two orders of magnitude higher when compared to that of trabecular bone and one order of magnitude higher when compared to cortical bone.

For this reason, orthopaedics components obtained in massive, bulk metal alloys cannot deform easily under the typical biological loads. In biological environment it is crucial for an orthopaedic component to be fully integrated in the surrounding bone tissue, in order to obtain a complete interconnection between implant and human body.

When a component with an high elastic modulus is used, stress shielding phenomena may occur, preventing the right interaction between implant and bone tissue. It is in fact important that the prosthetic implant transmits the applied load to the surrounding bone tissue, in order to prevent bone tissue reabsorption and thus loss of adhesion between implant and surrounding bone tissue.
Friction Coefficient

During the early clinical applications of Trabecular Titanium, it was observed by the surgeons that the prosthetic implants obtained in Trabecular Titanium showed a higher stability compared to conventional ones. This was supposed to be caused by the higher friction coefficient of the trabecular structure against the cortical and trabecular bone on which the prosthetic implant was applied.

It was later demonstrated by inclined plane experiments that Trabecular Titanium generated a Friction Coefficient higher than 0.8 against synthetic bone.

In order to evaluate the friction coefficient of the trabecular titanium structures at different load conditions, the testing apparatus of Figure 37 has been developed as a modulus added to the standard mechanical testing equipment. Using this modulus, an inextensible string is connected to the structure to be tested and to the crosspiece of the equipment.

The trabecular component lays on a panel of synthetic bone or on a slice of real bone in order to simulate the real coupling conditions. An heavy load is then put on the component and the string is pulled at increasing load until the component moves on the testing plane. Using this method, it is possible to estimate the friction coefficient of the trabecular structure as ratio between the normal load and the applied pulling load required to obtain the movement of the sample.
Increasing the normal load, it is possible to measure the friction coefficient developed by the trabecular structure and the counter structure as a function of the applied load and thus simulate the real conditions of application.

**Table 9: Friction coefficient results at high applied loads**

<table>
<thead>
<tr>
<th>Grade</th>
<th>Structure</th>
<th>Friction coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade 2</td>
<td>A</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>1.21</td>
</tr>
<tr>
<td>Grade 5</td>
<td>A</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Table 9 resumes the results obtained from the friction coefficient tests performed at higher normal loads (50 N) on the different structures, against bovine trabecular bone. As can be easily observed, all the structures show an extremely high friction coefficient, superior to 1, which can be associated with a strong mechanical interaction between the two surfaces.

**Figure 38: Wear tracks caused by Trabecular Titanium (B) on bone tissue**

Figure 38 clearly explains why the friction coefficient can reach values superior to 1. It can be observed the presence of wear tracks on the surface of the bone, which can be associated with asperities present on the trabecular structure that partially penetrate the bovine bone porosities, acting as anchors in order to increase the load required to move the sample. The higher the applied normal load, the higher the penetration of the asperities in the bone.
porosities, strongly increasing the load required to move the sample on the counter surface. The Structures C resulted to have increased friction coefficients compared to the other structures due to the bigger porosities and thus the reduced contact points between sample and counter surface resulting in a deeper penetration caused by a higher pressure. For the same reason, Structure B resulted to have higher friction coefficient compared to Structure A.
REFERENCES


5 - CONCLUSIONS

The experimental results reported in this study illustrated that with the application of EBM technology it is possible to obtain components having the following characteristics:

- The relative porosity of the three different structures are comparable to literature results for spongy bone and in particular in the case of Structure B and C;
- The structural voids dimension, especially pore size of the Structure B, is comparable with the values that can be found in literature for structures that improve osseointegration, while Structure A showed pores with similar diameter compared to human bone and Structure C showed pores larger than optimal values from literature; it remains to be determined whether the theoretical enhanced tissue ingrowth properties of Trabecular Titanium can provide long-term biological fixation in the clinical environment and therefore maximizing osseointegration of the prosthetic implant;
- The composition of the alloy is within the range of the values for biomedical Grade 2 titanium and the microstructure is homogeneous, as suggested by the Vickers micro-hardness test and as confirmed by the observation with optical microscopy on an etched sample. Both Grade 5 and Grade 2 titanium are in fact universally considered suitable for biomedical applications;
- All three structures in Trabecular Titanium and in particular structures obtained in Titanium Grade 2 showed limited mechanical properties, strongly influenced by the porosity percentage and the composition of the chosen alloy;
- The tension test used to prove adhesion showed that the cellular solid structure do not detach from the bulk dense material if they are both made with the same process;
- The elastic modulus of Trabecular Titanium, in particular for Structure B and C in both titanium alloys has proven to be close to that of human spongy bone. Trabecular Titanium sample A has shown a higher modulus, but still inferior to that of cortical bone;
- The high friction coefficient resulted to be fundamental for primary prosthesis stability during implant, improving the surgical implanting procedures.

The synergic combination of this highly porous pure titanium biomaterial and his mechanical properties together with potentially enhanced biological fixation of the prosthetic implants can allow the achievement of better clinical results when compared to conventional porous-coated acetabular components. The low rigidity of the Trabecular Titanium™ structure fosters the transmission of physiological loads from implant to bone. It is far more resistant compared to trabecular bone; therefore it can be used as ideal filler/support structure for bone ingrowth and consequently osseointegration of the implant. Clinical evidences in orthopaedic field are required to support the long-term stability of the prosthesis.
PART II:
NANOMETRIC COATINGS
OBTAINED BY ATOMIC LAYER DEPOSITION
1- Failures of Biomedical Materials

Biomaterials for prosthetic implant applications should possess sufficient mechanical strength to sustain the forces to which they are subjected (usually related to the weight of the patient) so that they do not undergo fracture and more importantly, a bio-implant should have very high corrosion and wear resistance in highly corrosive body environments and at varying loading conditions, apart from fatigue strength and fracture toughness.

A biomaterial should remain intact for a long period and should not fail until the death of the person. This requirement obviously demands a minimum service period about 15-20 years in older patients and more than 20 years for younger patients. The success of a biomaterial or an implant is highly dependent on three major factors:

- the properties (mechanical, chemical and tribological) of the biomaterial;
- the biocompatibility of the biomaterial;
- the health status of the patient.

The currently used materials that were selected based on above mentioned criteria although well-functioning in the human system are still found to generally fail within a period of about 12-15 years, which leads to revision surgery in order to regain the functionality of the system. The reasons for their failure are manifold which includes mechanical, chemical, tribological, surgical, manufacturing and biocompatibility issues. Out of all these issues, the failure of an implant due to corrosion or wear have remained two of the main challenging clinical problems [1-15].
REASONS FOR CORROSION FAILURES

Corrosion is a major problem in the complex and aggressive electrolytic environment of the human body [16]. The implants face severe corrosive environments which includes a wide list of constituents [17]. The aqueous media contained in the human body may consist of various anions such as chloride, phosphate, and bicarbonate ions, cations like Na⁺, K⁺, Ca²⁺, Mg²⁺ etc., organic substances of low-molecular-weight species as well as relatively high molecular-weight polymeric components, and dissolved oxygen, depending on different parameters such as location, inflammatory status and age of the patient [18, 19].

The various biological molecules also showed a clear effect in altering the equilibrium of the corrosion reactions at the implant surface by consuming the products due to anodic or cathodic reactions.

The electronic double layer formed at the surface of a metallic prosthetic implant may also result altered by the presence of proteins, which can easily bind themselves to metal ions and carry them away from the implant surface. In addition, proteins that are absorbed on the surface are also found to reduce the diffusion of oxygen at certain regions and cause preferential corrosion at those regions [16].

Hydrogen which is formed by cathodic reaction acts as a corrosion inhibitor, however, the presence of bacteria seems to change this behaviour and enhance corrosion by absorbing the hydrogen present in the vicinity of the implant [16]. Hydrogen may also affect the titanium surface in presence of tribo-corrosive phenomena, leading to a severe embrittlement of the biomaterial and thus to a mechanical failure of the component.

Alteration of the environmental pH values are also of major concern due to their influence on the corrosion behaviour of biomaterials, mainly due to the formation of a non-protective oxide layers at the surface of biomaterials at particularly high or low pH values. Though, the pH value of an unaltered human body environment is typically maintained at about 7.0, this value may change from about 3 to about 9 due to several causes such as accidents, imbalance in the biological system due to diseases, infections and other factors. The local pH value in proximity of the implant is also influenced by geometrical parameters (in presence of crevice the pH usually drops).

In spite of the fact that most of the materials used are protected from the environmental attack by the surface oxide layers (Cr oxides for Stainless Steel and Cobalt alloys, Titanium oxides for Titanium alloys), there is clinical evidence for the release of metal ions from the implants and this leaching has been attributed to corrosion and tribo-corrosion processes, probably caused by the synergetic action of the local acidification, the presence of Cl⁻ ions and the presence of Hydroxyapatite crystals which may cause wear and contribute to corrosion adding Ca and P ions to the solution. It has been well accepted that the tolerable corrosion rate for metallic implant systems should be about $2.5 \times 10^{-4}$ mm/yr, or 0.01 mils/yr [20].

The most common forms of corrosion that occur are uniform corrosion, intergranular, galvanic and stress corrosion cracking, pitting and fatigue corrosion. Even though new materials are continuously being developed to replace implant materials used in the past, clinical studies show
that these materials are also prone to corrosion to a certain extent [21]. The two physical characteristics which determine implant corrosion are thermodynamic forces which cause corrosion either by oxidation or reduction reaction and the kinetic barrier such as surface oxide layer which physically prevents corrosion reactions [21-23].

In some cases though the material will not fail directly due to corrosion, it is found to fail due to accelerated processes such as wear and fretting leading to tribocorrosion and thus electrochemically enhanced mechanical failures. Fretting is a surface mechanical fatigue phenomena which results in the rupture of protective oxide layer, initiation of cracks and formation of reactive metal atoms on the surface that are more susceptible to corrosion due to the previous removal of the natural protective oxide layer [24].

In order to limit further oxidation, initially formed passive films must have certain characteristics:

- It must be non-porous, in order to prevent contact between the electrolyte and the active metal underneath the surface;
- It must have an atomic structure that will limit the migration of ions and electrons across the metal oxide-solution interface;
- High abrasion resistance in order not to be easily removed when the biomaterial undergoes fretting or contact fatigue.

Hence, when a material is developed for implant application, it should not only be subjected to basic corrosion screening test, but also has to be tested for its behaviour under different conditions such as reciprocal wear, fretting, stress corrosion etc. depending on their applications. There are ASTM standards for testing corrosion resistance of these materials under different conditions. The commonly used standards for testing different corrosion processes are given in Table 10 [25]. Corrosion is accelerated in the presence of wear and also simultaneous corrosion and wear are often encountered in biomedical implants. Dearnley et al. have evaluated the corrosion behaviour of the scratched coated specimens to determine the wear accelerated corrosion behaviour of the coatings and also suggested a methodology to measure the simultaneous corrosion and wear of a material [26]. However it is important to note that there are no standards available to test the tribocorrosion behaviour of the implants.

<table>
<thead>
<tr>
<th>ASTM Standards</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM G61-86 and ASTM G 5-94</td>
<td>Corrosion performance of metallic biomaterials</td>
</tr>
<tr>
<td>ASTM G71-81</td>
<td>Galvanic corrosion in electrolytes</td>
</tr>
<tr>
<td>ASTM F46-87</td>
<td>Pitting or crevice corrosion of metallic surgical implant materials</td>
</tr>
<tr>
<td>ASTM F2129-01</td>
<td>Cyclic potentiodynamic polarization measurements</td>
</tr>
</tbody>
</table>

Surface oxide film formed on metallic materials plays an important role as an inhibitor for the release of metallic ions and the behaviour of the surface oxide changes with the release of ions. Further, the composition of the surface oxide film changes according to reactions between the
surfaces of metallic materials and living tissues. Even low concentration of dissolved oxygen, inorganic ions, proteins, and cells may accelerate the metal ion release. In addition, the dissolution of surface oxide film due to active oxygen species has also been reported [27]. The regeneration time of the surface oxide film after disruption also decides the amount of ions released. Tissue compatibility, the prerequisite for an implant is basically determined by the nature of the reactions which take place at the initial stages after implantation and thus the success of the implant depends on the reactions taking place between the surface of metallic materials and living tissues soon after the fixation of the implant.
AUSTENITIC STAINLESS STEEL

In the field of biomaterials for prosthetic implants, the most commonly employed steel alloys are without doubt the austenitic AISI 316 and AISI 316L grades. ASTM recommends type 316L for implant fabrications for the obvious reason that presence of less carbon decreases the chance of forming chromium carbide that generally results in intergranular corrosion. Lowering of the carbon content also makes this type of stainless steel more corrosion-resistant to chlorine-bearing solutions such as physiological saline in the human body [5]. Other common biomedical steels include martensitic AISI 420 and dual phase AISI 630, which are not actually applied for in-vivo implants due to their sensibly lower corrosion resistance caused by the presence of martensitic phase, which is extremely sensible to corrosion.

Stainless steel is susceptible to localized corrosion by chloride ions and reduced sulfur compounds [28]. The presence of micro organisms on a metal surface often leads to highly localized variations in the concentration of the electrolytic constituents, in the pH values and in the oxygen levels [29]. Studies on corrosion and electrochemical behavior of 316L Stainless Steel in the presence of aerobic iron-oxidizing bacteria (IOB) and anaerobic sulfate-reducing bacteria (SRB) reveal that the interactions between the stainless steel surface with the corroded products, bacterial cells and their metabolic products increases the corrosion damage and also accelerates pitting propagation [30]. In this respect, the antibacterial activity exhibited by different material may have an effect in limiting the bacterial related effects on the corrosion protection of implants. The decreasing antibacterial activity exhibited by different materials is given in the following order gold > titanium > cobalt > vanadium > aluminum > chromium > iron, with also silver and copper being considered as efficient antibacterial materials. Nevertheless, gold is only used in a limited array of biomedical applications due to the low mechanical properties and high density, while the other elements are usually present in form of oxides or alloyed with other elements, reducing their efficiency.

Studies on retrieved implants show that more than 90% of the failure of implants of 316L SS are due to pitting and crevice corrosion attack [31], which are also the most common failure causes in other industrial applications. These localized corrosion attacks also lead to a leaching of metallic ions from implants, which may have a toxic effect on the human body, in particular for Nickel ions. For these two reasons, AISI 316 L Stainless Steel necessitate improvement in the corrosion resistance by bulk alloying or surface modification techniques [32].

Biomedical materials which are subjected to cyclic loading and high stresses in the presence of aggressive environment fail due to fatigue [4, 6, 27]. Fatigue process is found to get further accelerated due to the formation of wear debris leading to fatigue wear. During fatigue there is
disruption of the oxide layer and the inability of the material to repassivate immediately exposes some region of the metal to the environment leading to corrosion. The initiation of crack due to fatigue was observed during the measurement of corrosion potential of cold worked 316L SS and it was also observed that the fatigue strength dropped drastically when the repassivation was suppressed, thus, confirming that oxide layer formation plays a vital role in the determination of the fatigue life of the materials exposed to aggressive corrosive environment [4]. In addition, fretting that occurs between implant and bone is also found to accelerate the fatigue as the repassivation becomes more difficult in the presence of fretting.

**Cobalt Alloys**

Cobalt alloys have a wide range of industrial applications, both as bulk or coating materials mainly due to their optimal tribological behaviour coupled with a good overall mechanical resistance. Biomedical cobalt based alloys (Co-Cr-Mo) have better mechanical strength, elastic modulus, abrasion resistance and corrosion resistance properties when compared to those of biomedical austenitic stainless steels. As with stainless steel, chromium is the alloying element which provides the essential corrosion resistance thanks to the formation of a non-porous nanometric superficial CrO$_2$ protective layer which acts as a barrier preventing contact between active metal and electrolytes. But in contrast to the austenitic stainless steels, also cobalt contributes to the corrosion resistance of the alloy, making cobalt-chromium based alloys excellent for their high corrosion resistance [33]. Because of their high mechanical properties, apart from those alloys being used for the fabrication of removable partial dentures, Cobalt alloys are also used for implants that require fine framework constructions [34]. Cobalt-based alloys have been widely employed in orthopaedic implants, but biocorrosion of this alloy is one of the major problems to be dealt with as a larger release of metal ions which causes adverse effects was observed [35].

Co-Cr-Mo alloy is used as a femoral head of joint prostheses in conjunction with an ultra high molecular weight polyethylene (UHMWPE) cup because of the high wear and corrosion resistance of this alloy. The problem with the metal-on-metal couple is that the release of metal ions is higher than that of the polymer-on-metal couple in vivo, which will, over many years lead to toxicity problem. The metal ions dissolved from Co-Cr-Mo alloy powder bind serum proteins to a much greater level compared to that of Ti-6Al-4V alloy. The conventional Co-29Cr-6Mo-1Ni alloy (ASTM F75-92) contains 1% in mass of Ni and the Ni and Co ions are responsible for allergic reactions. Reactions to contact with cobalt in an allergic individual mainly include inflammatory responses, allergic contact dermatitis and irritant dermatitis. Ni causes carcinogenicity and the decrement of Ni content in the Co-Cr-Mo alloy is one of the potential solutions that may be applied in order to solve the toxicity problem related to the application of cobalt nickel based systems [36].
Thanks to their high mechanical strength, low elastic modulus, relatively low density, and good combination of mechanical and corrosion resistance, the application of titanium and its alloys have reached a large widespread in different biologically related applications, especially for prosthetic implant components [37] since they possess an higher strength to weight ratio when compared to austenitic stainless steels or cobalt alloys. Initially, both commercially pure titanium and its biomedical alloys were supposed to be completely inert and immune to corrosion in all biological environments, and thus they resulted to be the only mechanical resistant materials to be completely biocompatible [38]. Titanium and in particular titanium alloys corrosion resistance is strongly related to the stability of the Titanium Oxide layer which is formed on the exterior surface of Titanium components (5-7 nm) and which acts as a barrier. When this oxide layer is compromised, both for a mechanical action (fretting, surface fatigue) or a chemical action (acid environments with low oxygen contents), the good corrosion resistance is drastically reduced. This in particular may affect titanium due to its low tribological resistance which easily leads to an intense localized damage of the superficial titanium oxide.

As of now, for their high corrosion resistance and low elastic modulus, titanium and titanium alloys are widely used in prosthetic implants for joint replacements, bone fixation structures, screws and components, dental implants, heart pacemakers, artificial heart valves, stents and components in high-speed blood centrifuges. Nevertheless, these implants such as artificial joints and bone plates are likely to be damaged mostly due to fatigue [39] and fretting [40, 41].

Even the actually widely used Ti-6Al-4V (Grade 5) alloy has clearly shown potential health dangers: in recent research studies it was shown that the release of aluminium and vanadium ion from the alloy may lead to Alzheimer disease, osteomalacia and peripheral neuropathy. Vanadium oxides ($V_2O_5$) toxicity was also demonstrated and both oxides and metallic vanadium presences have been demonstrated [42]. Further, Ti-6Al-4V alloy has a lower wear resistance when compared to other biomedical alloys and an higher elastic modulus when compared to bone which may leads to “stress shielding effect” [42, 43]. Another clinical concern with titanium and its alloys is because of the particles released due to the breakdown of oxide layer associated with metal implant degradation.

In the last few decades, new titanium alloys have been developed for applications in biological environments, such as Nb-based Titanium alloys that, thanks to the formation of Nb-rich pentoxide, show higher corrosion resistance in biological environments [44]. Similar effects were obtained with the addition of Tantalium (Ta) which, thanks to the formation of $Ta_2O_5$ highly stable oxides, greatly reduced the concentration of metal release and enhanced the corrosion resistance of the alloy [45]. Thus the corrosion resistance of the passive film is very much dependent on the thickness of the layer formed and the nature of the elements present in titanium and its alloys [14]. The corrosion of NiTi alloys used for dental, orthopaedic and cardiovascular applications is debatable as there are conflicting reports on their corrosion resistance when compared to Cp Ti or Ti-6Al-4V. Many studies have shownthat NiTi is highly compatible with living tissues but adverse effects caused by this material are also often reported.

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particular, severe cell death arising from the poor corrosion resistance and toxic constituents such as Ni in NiTi alloys has been observed [46]. Though this alloy exhibits high corrosion resistance to pitting tested at passive conditions and also potentiodynamic test at normal ranges of pH and temperatures corresponding to human body, there are reports which show the inferior corrosion behavior of this alloy when compared to Ti-6Al-4V and also stainless steel based materials.

MAGNESIUM ALLOYS

Thanks to the complete bio-solubility and the absence of a toxicity level, a part from when renal failure prevents urinary excretion, recently magnesium alloys are emerging as the better alternative for temporary implant devices and as the main constituent material for stents [5]. As the currently used permanent cardiovascular implants pose several problems such as thrombogenicity, permanent physical irritation, mismatches in mechanical behaviour between stented and non-stented vessel area etc., a new domain of research on metallic and polymeric implants focuses on new biodegradable implants, which have the ability to completely dissolve in biological environment after a certain, opportunely tailored amount of time of functional use. Magnesium as a degradable implant material provides both biocompatibility and suitable mechanical properties compared to other biodegradable materials such as biopolymers both in in vitro and in-vivo studies and it has been shown that magnesium is suitable to be used for degradable implants as they exhibit good cell attachment and tissue growth [5, 66, 67]. However the studies concerning the corrosion behaviour of magnesium in biological environment and cytotoxicity of magnesium are lacking. Recently, a number of studies have been carried out to investigate the corrosion behaviour of magnesium alloys in artificial physiological fluids and most of them are Al containing Mg alloys [68]. Most alloying elements will dissolve into the human body during the magnesium alloy degradation, for example, when the AZ91D magnesium alloy is used, the Al present in the alloy would get into the human body, which might be hazardous, from the health point of view. The magnesium alloy implants are expected not to degrade until the healing is completed and tissue growth has occurred. However it is unfortunate to observe that magnesium and its alloys corrode too quickly at the physiological pH of 7.2 to 7.4 as well as in physiological media containing high concentrations of aggressive ions, thereby loosing mechanical integrity before the tissues have sufficient time to heal [69]. Various methods such as alkali heat treatment [70], plasma immersion ion implantation (PIII) [71], micro-arc oxidation (MAO) [72], and anodic oxidation [73] have been proposed to improve the corrosion resistance of Mg alloys. Thus Mg systems open a new window in the field of cardiovascular implants.
**Biological fretting of common biomaterial alloys**

The majority of corrosion-resistant engineering materials rely on passivity for their protection, in particular in the medical and orthopaedic field, in which the environment can be considered aggressive for most metallic alloys. The three main passive metallic implant materials are titanium-based alloys, austenitic stainless steels and cobalt-based alloys.

The oxide film formation is of great importance for these three families of surgical-grade implant materials, and its stability and protection is usually not compromised by the aggressive biological environment. Wear phenomena, in particular fretting, may disrupt the protective passive films formed on the orthopaedic devices, leading to a release of heavy-metals ions into the surrounding tissues, with a consequent inflammatory response [37].

Wear phenomena are mainly concentrated on joint replacement prosthetic components, in which tribological damage may occur due to the high loads applied and the reciprocal sliding of the joint coupling. This usually leads to an uniform wear over time of the tribological surfaces which, thanks to the application of modern materials, is limited.

Fretting occurs when two surfaces in contact are put in relative motion, with “small” relative displacements. This results in “damage” to both surfaces in the contact region. If one or both the surfaces are additionally under cyclic load, then both may experience fretting fatigue. This tribological damage can be extremely intense and lead to mechanical failures of the component in a limited amount of time when compared to conventional wear.

Fretting fatigue is usually encountered in riveted, pinned or threaded connections, clamped components, press-fitted joints, splines, etc. Not only fastened joints, but also bearings, rotors, gears and orthopaedic implants fail from fretting fatigue, which may also be enhanced by corrosion [38].

Fretting is a time-dependant process. When acting alone, it can have a significant effect on functional capability, performance and structural integrity as well as appearance. When acting in conjunction with cyclic loads, it is possible that cracks nucleate in regions of fretting damage. This kind of potentially deleterious process frequently occurs at joints of all types. If it occurs, fretting can produce cracks, and the environment and/or contact conditions may accelerate the propagation of cracks by the cyclic loads [39]. Fretting is in fact viewed as a nucleation and early growth fatigue crack acceleration process [40-42].

In literature [43-47], a lot of effort was made in order to explain the damage production of the fretting fatigue processes. The initial stage of the fretting fatigue is considered to be the contact adhesion between the two tribological surfaces due to the intense loads applied and the presence of surface asperities. Most cracks are supposed to be nucleated during this phase of the phenomenon. The asperities may then break apart, creating fretting debris and causing oxidation and eventually corrosion of the metal underneath. In prosthetic implants, the presence of crevices in proximity of the contact areas may also lead to intense corrosion due to local lowering of the pH values of the biological environment and the presence of nucleated
cracks on the surface may lead to cyclic oxidation/fracture phenomena of the material inside the crack, promoting the mechanical failure of the component.

**Stainless Steel**

Back in 1969 [48], it was already observed that 90% of the implants made in AISI 316 Stainless Steel showed corrosion phenomena when removed from the body. Fretting corrosion, in particular, was observed in the majority of these components. In particular, it was observed [49] that the main cause of corrosion at screw-plate interfaces and other shielded sites of surgical implants was fretting and not the crevice corrosion which was also observed on non-stressed components. Also localized surface corrosion defects were observed in hip-nail plate assemblies made of type 316 Stainless Steel, with matching screws and the damage was attributed to fretting corrosion, a combination of abrasive, corrosive and adhesive wear [50].

**Cobalt Alloys**

Co-Cr-Mo biomedical alloys were observed to have a lower wear rate when compared to 316 Stainless Steel in physiological saline solutions [51]. Kumagai et al. [52], shown that Ni-free Cobalt alloys show superior tribological property in reciprocating sliding wear, when compared to Titanium alloys. It also resulted from the work of Iwabuchi et al. [53] that the contribution of electrochemical factors on Co-alloys and Ti-alloys is about 50% of the total fretting wear, while for SUS304 Stainless Steel it resulted to be around 80%. In total hip replacement femoral modular components made of Cobalt alloys, it was observed that body fluids penetrate in the locking mechanisms facilitating mechanically assisted crevice and fretting corrosion [54-56]. Implant retrieval studies have implicated modular junction fretting as significant, if not primary, source of metal release [57-59] for Cobalt alloy components.

**Titanium Alloys**

Due to its intrinsic low tribological characteristics, titanium alloys wear resistance has been deeply investigated in literature in the last two decades, often trying to protect the metallic substrate with a ceramic coating or a diffusive treatment. In general, as already observed for Stainless Steel and Cobalt alloys, it was observed that corrosion is an accelerating factor on the wear behaviour [60]. Fretting fatigue failures of uncoated titanium alloys resulted to be characterized by formation of oxides due to generation of high temperature from friction [61]. The damage severity resulted to be very high in particular for Titanium/Titanium coupling due to metallurgical compatibility and enhanced by the presence of saline fluids. Using orientation
image microscopy, it resulted that fretting produce a significant increase in low angle misorientation in a region near the fretted surface for titanium alloys, implying a fretting-induced microstructure evolution [62]. From the literature data, it seems that titanium alloys always require a surface treatment or a coating in order to be applied as a biomaterial in fretting conditions.
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[46] L. Vincent, Materials and Fretting, presented at Int. Conf. on Fretting Fatigue, Sheffield, UK, (1993);


2 - PROTECTIVE TREATMENTS FOR BIOMEDICAL ALLOYS

A wide array of completely different techniques have been used in literature in order to improve the resistance of biomedical materials to both chemical aggression (corrosion) and mechanical damaging (wear).

These techniques may be based on different principles:

- **Coating the biomedical material** to improve the hardness, reduce the friction coefficient and create a barrier against the penetration of aggressive electrolytes. This can be obtained by means of a hard, ceramic layer, using Physical Vapour Deposition, Ion Beam Assisted Deposition, Atomic Layer Deposition or Sol-Gel coatings;

- **Diffusing reinforcing elements into the biomedical material**, in order to obtain a microstructural modification (carburized steel) or precipitation of hard particles and reinforcing second phases (nitrided steel). This can be obtained by means of carburizing, nitriding, boronizing or ion implantation.

In this chapter, part of these techniques have been reviewed and conventional biomedical applications have been briefly investigated and discussed.
Carburizing, is a heat treatment process in which iron or steel is heated in the presence of another material (in the range of 900 to 950 °C (1,650 to 1,740 °F)) which liberates carbon as it decomposes. Depending on the amount of time and temperature, the affected area can vary in carbon content. Longer carburizing times and higher temperatures lead to greater carbon diffusion into the part as well as increased depth of carbon diffusion. When the iron or steel is cooled rapidly by quenching, the higher carbon content on the outer surface becomes hard via the transformation from austenite to martensite, while the core remains soft and tough as a ferritic and/or pearlite microstructure.

This manufacturing process can be characterized by the following key points: It is applied to low-carbon workpieces; workpieces are in contact with a high-carbon gas, liquid or solid; it produces a hard workpiece surface; workpiece cores largely retain their toughness and ductility; and it produces case hardness depths of up to 0.25 inches (6.4 mm).

Carburization of steel involves a heat treatment of the metallic surface using a source of carbon. Early carburization used a direct application of charcoal packed onto the metal (initially referred to as case hardening), but modern techniques apply carbon-bearing gases or plasmas (such as carbon dioxide or methane). The process depends primarily upon ambient gas composition and furnace temperature, which must be carefully controlled, as the heat may also impact the microstructure of the rest of the material. For applications where great control over gas...
composition is desired, carburization may take place under very low pressures in a vacuum chamber.

Plasma carburization is increasingly used in major industrial regimes to improve the surface characteristics (such as wear and corrosion resistance, hardness and load-bearing capacity, in addition to quality-based variables) of various metals, notably stainless steels. The process is used as it is environmentally friendly (in comparison to gaseous or solid carburizing). It also provides an even treatment of components with complex geometry (the plasma can penetrate into holes and tight gaps), making it very flexible in terms of component treatment.

The process of carburization works via the implantation of carbon atoms into the surface layers of a metal. As metals are made up of atoms bound tightly into a metallic crystalline lattice, the implanted carbon atoms force their way into the crystal structure of the metal and either remain in solution (dissolved within the metal crystalline matrix — this normally occurs at lower temperatures) or react with the host metal to form ceramic carbides (normally at higher temperatures, due to the higher mobility of the host metal's atoms). Both of these mechanisms strengthen the surface of the metal, the former by causing lattice strains by virtue of the atoms being forced between those of the host metal and the latter via the formation of very hard particles that resist abrasion. However, each different hardening mechanism leads to different solutions to the initial problem: the former mechanism — known as solid solution strengthening — improves the host metal's resistance to corrosion whilst imparting its increase in hardness; the latter — known as precipitation strengthening — greatly improves the hardness but normally to the detriment of the host metals corrosion resistance. Engineers using plasma carburization must decide which of the two mechanisms matches their needs. Gas carburizing is normally carried out at a temperature within the range of 900 to 950 °C. In oxy-acetylene welding, a carburizing flame is one with little oxygen, which produces a sooty, lower-temperature flame. It is often used to anneal metal, making it more malleable and flexible during the welding process.

A main goal when producing carbonized workpieces is to insure maximum contact between the workpiece surface and the carbon-rich elements. In gas and liquid carburizing, the workpieces are often supported in mesh baskets or suspended by wire. In pack carburizing, the workpiece and carbon are enclosed in a container to ensure that contact is maintained over as much surface area as possible. Pack carburizing containers are usually made of carbon steel coated with aluminum or heat-resisting nickel-chromium alloy and sealed at all openings with fire clay.

There are different types of elements or materials that can be used to perform this process, but these mainly consist of high carbon content material. A few typical hardening agents include carbon monoxide gas (CO), sodium cyanide and barium chloride, or hardwood charcoal. In gas carburizing, the CO is given off by propane or natural gas. In liquid carburizing, the CO is derived from a molten salt composed mainly of sodium cyanide (NaCN) and barium chloride (BaCl). In pack carburizing, carbon monoxide is given off by coke or hardwood charcoal.

In the case of titanium, the hardening effect is not obtained due to a microstructural modification of the alloy, but due to the precipitation of titanium carbides and, eventually, the
formation of a non-stoichiometric TiC superficial layer. Carburizing of titanium is often obtained by plasma or laser technologies. The highly energetic heat sources can be explained by the fact that, even if titanium has a strong tendency to react with Carbon, the diffusivity of Carbon in Titanium Carbide is many orders of magnitude lower than diffusivity of Carbon in Titanium. For this reason, after a nanometric layer of TiC has been formed on the surface of Titanium, the process slows down rapidly and very long exposure times are required to diffuse new Carbon inside Titanium. The diffusive process is temperature dependant, but too high temperatures might compromise the heat treatments of the bulk titanium component and thus must be avoided if possible. For this reason, the use of concentrated energy surces such as plasmas, electron beams and laser beams can be successfully used in order to obtain a diffusive treatment without increasing the temperature.

The main characteristics of the carburizing treatments applied in the biomedical field for the protection of prosthetic implants are presented on Table 11:

<table>
<thead>
<tr>
<th>Treatment Characteristics</th>
<th>Literature references: [1-3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomedical alloys treated:</td>
<td>Titanium alloys</td>
</tr>
<tr>
<td>Typical temperature:</td>
<td>&gt;700 °C, or plasma/laser/electron beam techniques must be used as an energy source</td>
</tr>
<tr>
<td>Typical Thickness:</td>
<td>2~10 μm</td>
</tr>
<tr>
<td>Treatment time:</td>
<td>1~10 h</td>
</tr>
<tr>
<td>Influence of geometry:</td>
<td>Limited penetration in hollow parts</td>
</tr>
<tr>
<td>Corrosion:</td>
<td>Not deeply investigated</td>
</tr>
<tr>
<td>Wear:</td>
<td>Increased hardness, wear resistance, fatigue resistance</td>
</tr>
<tr>
<td>Main advantages:</td>
<td>Relatively cheap treatment</td>
</tr>
<tr>
<td>Main disadvantages:</td>
<td>Not suited for all biomedical alloys, must be specifically calibrated on the chemical composition, sample displacement during treatment may be necessary, in particular when lasers and electron beams are used as an energy sources.</td>
</tr>
</tbody>
</table>
Nitriding

Nitrided steel are used in a wide range of applications: such as gears, crankshafts, camshafts, cam followers, valve parts, extruder screws, die-casting tools, forging dies, extrusion dies, injectors and plastic-mold tools. The processes are named after the medium used to donate nitrogen. The three main methods used are: gas nitriding, salt bath nitriding, and plasma nitriding. In gas nitriding the donor is a nitrogen rich gas, usually ammonia (NH\(_3\)), which is why it is sometimes known as ammonia nitriding. When ammonia comes into contact with the heated work piece it disassociates into nitrogen and hydrogen. The nitrogen then diffuses from the surface into the core of the material. This process has been around for nearly a century though only in the last few decades has there been a concentrated effort to investigate the thermodynamics and kinetics involved. Recent developments have led to a process that can be accurately controlled. The thickness and phase constitution of the resulting nitriding layers can be selected and the process optimized for the particular properties required. In salt bath nitriding the nitrogen donating medium is a nitrogen containing salt such as cyanide salt. The salts used also donate carbon to the workpiece surface making salt bath a nitrocarburizing process. The temperature used is typical of all nitrocarburizing processes: 550–590 °C (1022–1094 °F). When possible, salt bath nitriding is avoided due to the high toxicity of the salts used during the process. In plasma nitriding, the reactivity of the nitriding media is not due to the temperature but to the gas ionized state. In this technique intense electric fields are used to generate ionized molecules of the gas around the surface to be nitrided. Such highly active gas
Part II - Chapter 2: Protective treatments for Biomedical Alloys

with ionized molecules is called plasma, naming the technique. The gas used for plasma nitriding is usually pure nitrogen, since no spontaneous decomposition is needed (as is the case of gas nitriding with ammonia). There are hot plasmas typified by plasma jets used for metal cutting, welding, cladding or spraying. There are also cold plasmas, usually generated inside vacuum chambers, at low pressure regimes.

Usually steels are very beneficially treated with plasma nitriding. Plasma nitriding advantage is related to the close control of the nitrided microstructure, allowing nitriding with or without compound layer formation. Not only the performance of metal parts gets enhanced but working lifespan gets boosted. So does the strain limit, and the fatigue strength of the metals being treated. For instance, mechanical properties of austenitic stainless steel like wear can be significantly reduced and the hardness of tool steels can be double on the surface.

A plasma nitrided part is usually ready for use. It calls for no machining, or polishing or any other post-nitriding operations. Thus the process is user-friendly, saves energy since it works fastest, and causes little or no distortion.

This process was invented by Dr. Bernhardt Berghaus of Germany who later settled in Zurich to escape persecution of his community by the Nazis in 1939. It was only after his death in late 1960s that the process was acquired by Klockner group and popularized world over.

Plasma nitriding is often coupled with physical vapor deposition (PVD) process and labelled Duplex Treatment, to avail of immensely enhanced benefits. Many users prefer to have a plasma oxidation step combined at the last phase of processing to generate a smooth jetblack layer of oxides which is very resistant to not only wear but corrosion too.

Since nitrogen ions are made available by ionization, differently from gas or salt bath, plasma nitriding efficiency does not depend on the temperature. Plasma nitriding can thus be performed in a broad temperature range, from 260°C to more than 600°C. For instance, at moderate temperatures (like 420°C), stainless steels can be nitried without the formation of chromium nitride precipitates and hence maintaining their corrosion resistance properties.

In plasma nitriding processes nitrogen gas (N\textsubscript{2}) is usually the nitrogen carrying gas. Other gasses like hydrogen or Argon are also used. Indeed, Argon and H\textsubscript{2} can be used before the nitriding process during the heating up of the parts in order to clean the surfaces to be nitried. This cleaning procedure effectively removes the oxide layer from surfaces and may remove fine layers of solvents that could remain. This also helps the thermal stability of the plasma plant since the heat added by the plasma is already present during the warm up and hence once the process temperature is reached the actual nitriding begins with minor heating changes. For the nitriding process H\textsubscript{2} gas is also added in order keep the surface clear of oxides. This effect can be observed by analysing the surface of the part under nitriding.

Due to the high reactivity of Titanium with Nitrogen, Titanium nitriding is often industrially applied in order to obtain a hardening effect on Titanium components. As for Titanium carburizing, the initial formation of a TiN superficial layer strongly reduces the diffusion rate of nitrogen in Titanium and thus high temperatures or really long treatment times are required in
order to obtain a deep diffusion. To reduce both temperature and treatment time, processes involving high energetic sources, such as plasma, laser or electron beam, are often used.

The main characteristics of the nitriding treatments applied in the biomedical field for the protection of prosthetic implants are presented on Table 12:

<table>
<thead>
<tr>
<th>Treatment Characteristics</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Literature references:</td>
<td>[4-10]</td>
</tr>
<tr>
<td>Biomedical alloys treated:</td>
<td>Titanium alloys, Stainless Steel, Cobalt alloys</td>
</tr>
<tr>
<td>Typical temperature:</td>
<td>300-1100 °C, typically with plasma/laser/electron beam techniques in order to lower the treatment temperature</td>
</tr>
<tr>
<td>Typical Thickness:</td>
<td>2~10 μm</td>
</tr>
<tr>
<td>Treatment time:</td>
<td>~10 h</td>
</tr>
<tr>
<td>Influence of geometry:</td>
<td>Limited penetration in hollow parts</td>
</tr>
<tr>
<td>Corrosion:</td>
<td>Increased thanks to the formation of a superficial nitride layer (in particular for Titanium alloys)</td>
</tr>
<tr>
<td>Wear:</td>
<td>Increased hardness, wear resistance, fatigue resistance may be reduced in conventional treatments but enhanced using plasma or laser</td>
</tr>
<tr>
<td>Main advantages:</td>
<td>Relatively cheap treatment</td>
</tr>
<tr>
<td>Main disadvantages:</td>
<td>Must be specifically calibrated on the chemical composition, fatigue resistance is increased only for highly expansive treatments</td>
</tr>
</tbody>
</table>
Ion implantation is a materials engineering process by which ions of a material are accelerated in an electrical field and impacted into another solid. This process is used to change the physical, chemical, or electrical properties of the solid. Ion implantation is used in semiconductor device fabrication and in metal finishing, as well as various applications in materials science research. The ions can introduce both a chemical change in the target, in that they can introduce a different element than the target or induce a nuclear transmutation, and a structural change, in that the crystal structure of the target can be damaged or even destroyed by the energetic collision cascades.

Ion implantation equipment typically consists of an ion source, where ions of the desired element are produced, an accelerator, where the ions are electrostatically accelerated to a high energy, and a target chamber, where the ions impinge on a target, which is the material to be implanted. Thus ion implantation is a special case of particle radiation. Each ion is typically a single atom or molecule, and thus the actual amount of material implanted in the target is the integral over time of the ion current. This amount is called the dose. The currents supplied by implanters are typically small (microamperes), and thus the dose which can be implanted in a
reasonable amount of time is small. Therefore, ion implantation finds application in cases where
the amount of chemical change required is small.

Typical ion energies are in the range of 10 to 500 keV (1,600 to 80,000 aJ). Energies in the range
1 to 10 keV (160 to 1,600 aJ) can be used, but result in a penetration of only a few nanometers
or less. Energies lower than this result in very little damage to the target, and fall under the
designation ion beam deposition. Higher energies can also be used: accelerators capable of 5
MeV (800,000 aJ) are common. However, there is often great structural damage to the target,
and because the depth distribution is broad, the net composition change at any point in the
target will be small.

The energy of the ions, as well as the ion species and the composition of the target determine
the depth of penetration of the ions in the solid: A monoenergetic ion beam will generally have a
broad depth distribution. The average penetration depth is called the range of the ions. Under
typical circumstances ion ranges will be between 10 nanometers and 1 micrometer. Thus, ion
implantation is especially useful in cases where the chemical or structural change is desired to
be near the surface of the target. Ions gradually lose their energy as they travel through the
solid, both from occasional collisions with target atoms (which cause abrupt energy transfers)
and from a mild drag from overlap of electron orbitals, which is a continuous process. The loss of
ion energy in the target is called stopping and can be simulated with the binary collision
approximation method.

Nitrogen or other ions can be implanted into a tool steel target (drill bits, for example). The
structural change caused by the implantation produces a surface compression in the steel, which
prevents crack propagation and thus makes the material more resistant to fracture. The
chemical change can also make the tool more resistant to corrosion.

The main characteristics of the ion implantation treatments applied in the biomedical field for
the protection of prosthetic implants are presented on Table 13:

<table>
<thead>
<tr>
<th>TABLE 13: CHARACTERISTICS OF ION IMPLANTATION TREATMENTS FOR BIOMEDICAL ALLOYS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Treatment Characteristics</strong></td>
</tr>
<tr>
<td>Literature references: [11-16]</td>
</tr>
<tr>
<td>Biomedical alloys treated: Titanium alloys, Stainless Steel, Cobalt alloys</td>
</tr>
<tr>
<td>Implanted ions: N, Ca, Kr, Ar, O, P, Na, in order to obtain osteointegration, corrosion resistance, tribological resistance</td>
</tr>
<tr>
<td>Typical Thickness: 10~500 nm</td>
</tr>
<tr>
<td>Treatment time: ~4 h</td>
</tr>
<tr>
<td>Influence of geometry: Strongly dependant on the sample geometry, only perpendicular parts (respect to the ion source) can be treated</td>
</tr>
<tr>
<td>Corrosion: Corrosion resistance, may decrease or increase</td>
</tr>
</tbody>
</table>
### Chapter 2: Protective treatments for Biomedical Alloys

<table>
<thead>
<tr>
<th>Wear:</th>
<th>May increase hardness due to the formation of hard precipitates, but mainly due to lattice modifications. The effect is usually localized.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main advantages:</td>
<td>Almost any kind of ion may be implanted, depending on the different needs, it may also be coupled with other techniques.</td>
</tr>
<tr>
<td>Main disadvantages:</td>
<td>Expansive and only localized thicknesses of material may be influenced.</td>
</tr>
</tbody>
</table>
Physical Vapor Deposition

Figure 42: Scheme of PVD treatment chamber

Physical vapor deposition (PVD) is a variety of vacuum deposition and is a general term used to describe any of a variety of methods to deposit thin films by the condensation of a vaporized form of the material onto various surfaces (e.g., onto semiconductor wafers). The coating method involves purely physical processes such as high temperature vacuum evaporation or plasma sputter bombardment rather than involving a chemical reaction at the surface to be coated as in chemical vapor deposition. The term physical vapor deposition appears originally in the 1966 book Vapor Deposition by CF Powell, JH Oxley and JM Blocher Jr, but Michael Faraday was using PVD to deposit coatings as far back as 1838.

Variants of PVD include, in order of increasing novelty:

Cathodic Arc Deposition: In which a high power arc discharged at the target material blasts away some into highly ionized vapor.

Electron beam physical vapor deposition: In which the material to be deposited is heated to a high vapor pressure by electron bombardment in "high" vacuum.

Evaporative deposition: In which the material to be deposited is heated to a high vapor pressure by electrically resistive heating in "low" vacuum.

Pulsed laser deposition: In which a high power laser ablates material from the target into a vapor.
Sputter deposition: In which a glow plasma discharge (usually localized around the "target" by a magnet) bombards the material sputtering some away as a vapor. Here is an animation of a generic PVD sputter tool: PVD Animation

PVD is used in the manufacture of items including semiconductor devices, aluminized PET film for balloons and snack bags, and coated cutting tools for metalworking. Besides PVD tools for fabrication special smaller tools mainly for scientific purposes have been developed. They mainly serve the purpose of extreme thin films like atomic layers and are used mostly for small substrates.

The main characteristics of the PVD treatments applied in the biomedical field for the protection of prosthetic implants are presented on Table 15:

<table>
<thead>
<tr>
<th>Treatment Characteristics</th>
<th>Characteristics of ion implantation treatments for biomedical alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>Literature references:</td>
<td>[22-25]</td>
</tr>
<tr>
<td>Biomedical alloys treated:</td>
<td>Titanium alloys, Stainless Steel, Cobalt alloys</td>
</tr>
<tr>
<td>Deposited coatings:</td>
<td>TiN, TiCN, CrN, TiC</td>
</tr>
<tr>
<td>Typical Thickness:</td>
<td>1-5 µm</td>
</tr>
<tr>
<td>Treatment time:</td>
<td>~6 h</td>
</tr>
<tr>
<td>Influence of geometry:</td>
<td>Not effective in deep hollow parts, depends on the distance from the cathode</td>
</tr>
<tr>
<td>Corrosion:</td>
<td>Corrosion resistance is usually increased, even if defective layers may lead to increased localized corrosion</td>
</tr>
<tr>
<td>Wear:</td>
<td>Wear resistance is usually increased for relatively low applied loads, but for titanium and stainless steel, PVD fail under heavy loads due to the insufficient substrate hardness</td>
</tr>
<tr>
<td>Main advantages:</td>
<td>Relatively cheap treatment, many coating compositions can be deposited</td>
</tr>
<tr>
<td>Main disadvantages:</td>
<td>Expansive and only localized thicknesses of material may be influenced</td>
</tr>
</tbody>
</table>
Ion beam assisted deposition or IBAD or “IAD” (not to be confused with ion beam induced deposition, IBID) is a materials engineering technique which combines ion implantation with simultaneous sputtering or another physical vapor deposition technique. Besides providing independent control of parameters such as ion energy, temperature and arrival rate of atomic species during deposition, this technique is especially useful to create a gradual transition between the substrate material and the deposited film, and for depositing films with less built-in strain than is possible by other techniques. These two properties can result in films with a much more durable bond to the substrate. Experience has shown that some meta-stable compounds like cubic boron nitride (c-BN), can only be formed in thin films when bombarded with energetic ions during the deposition process.

Additional processing gases (N₂, CH₄, C₂H₂,...) can be added in the deposition chamber in order to obtain thin coating depositions on the surface, as the gases will get ionized and then accelerated through the surface by the ion source. Different gases may also be used at different times in order to obtain tailored multilayer structures.

The main limitation of IBAD technique is related to geometry of the substrate. As the IBAD deposition involves two different beams, the substrates must have a plain geometry. For some geometric configurations, such as cylindrical samples, spheres or hollow cavities, IBAD deposition will only be possible using a rotating support.
IBAD localized surface treatment can be efficiently used to partially coat components in which other treatments will lead to an undesired complete surface coverage.

The main characteristics of IBAD treatments applied in the biomedical field for the protection of prosthetic implants are presented on Table 14:

**Table 15: Characteristics of IBAD treatments for biomedical alloys**

<table>
<thead>
<tr>
<th>Treatment Characteristics</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Literature references:</td>
<td>[17-21]</td>
</tr>
<tr>
<td>Biomedical alloys treated:</td>
<td>Titanium alloys, Stainless Steel</td>
</tr>
<tr>
<td>Deposited coatings:</td>
<td>anti wear: Al₂O₃, TiN, TiCN, TiAIN, CrN, lubricant: MoS, osteointegrative: CaO, HA, antibacterial: Ag, Au, Cu, Zn</td>
</tr>
<tr>
<td>Typical Thickness:</td>
<td>0.5~5 µm</td>
</tr>
<tr>
<td>Treatment time:</td>
<td>~6 h</td>
</tr>
<tr>
<td>Influence of geometry:</td>
<td>Strongly dependant on the sample geometry, only perpendicular parts (respect to the ion source) can be treated</td>
</tr>
<tr>
<td>Corrosion:</td>
<td>Corrosion resistance is usually increased by ceramic coatings, but decreased by metallic coatings</td>
</tr>
<tr>
<td>Wear:</td>
<td>Increased by the application of ceramic coatings, even if defects leading to cracks and delamination were observed when applied on low hardness substrates</td>
</tr>
<tr>
<td>Main advantages:</td>
<td>Versatile. The application of IBAD results in improved adhesion thanks to the intensive energy beam</td>
</tr>
<tr>
<td>Main disadvantages:</td>
<td>Expansive and geometry-limited</td>
</tr>
</tbody>
</table>
**Atomic Layer Deposition (ALD)**

Atomic layer deposition (ALD) is a thin film deposition technique that is based on the sequential use of a gas phase chemical process. The majority of ALD reactions use two chemicals, typically called precursors. These precursors react with a surface one-at-a-time in a sequential manner. By exposing the precursors to the growth surface repeatedly, a thin film is deposited.

ALD is a self-limiting (the amount of film material deposited in each reaction cycle is constant), sequential surface chemistry that deposits conformal thin-films of materials onto substrates of varying compositions. ALD is similar in chemistry to chemical vapor deposition (CVD), except that the ALD reaction breaks the CVD reaction into two half-reactions, keeping the precursor materials separate during the reaction.

The possible application of ALD for the protection of biomedical alloys is still unexplored, and for this reason, Part 2 of the present thesis is centered on the application of ALD for the protection of biomedical alloys, and in particular AISI 316 L, which resulted to be the most corrosion sensitive biomedical alloy.

A more complete description of ALD will be presented in Chapter 3.
REFERENCES


- Part II -

Chapter 2: Protective treatments for Biomedical Alloys
3 - INTRODUCTION TO ALD

Atomic Layer Deposition (ALD) or Atomic Layer Epitaxy (ALE) is a layer-by-layer deposition technique which was introduced and developed to grow layers of semiconductor materials with controlled composition. Although the technique is well established at laboratory level and of great interest for a vast number of industrial sectors, its industrial applications are still rather limited, even if thickness and composition control of the deposited layer are strictly possible, and there is the possibility to, at least theoretically, obtain a complete substrate coverage including narrow porosities and hollows. The main fields of industrial interest are:

- **Biomedical:** biomimesis of components, corrosion protection of prosthesis, wear minimizing in biological environments, chemical barriers to ion release, promotion of osteointegration, and encapsulation;
- **Energetic:** photovoltaic layers, light reflectors, corrosion protection of components, hydrophilic or hydrophobic coatings, anti-dust coatings;
- **Electronic and microelectronics:** corrosion and wear protection of parts, components and connections, layers of memory devices, parts of screens, and nanocomponents;
- **Micromechanics:** not invasive nanometric protective coatings against corrosion and wear;
- **Optical applications:** reflective and transmitting coatings, lens protection, light filters, etc.;
- **Catalysis:** catalyzer coatings for membranes and porous structures.

The compositional, optical, mechanical, tribological and protective properties of ALD coatings can in fact be precisely tailored on the application requirements, mainly varying four parameters: the type and composition of the two precursor gases, the number of applied ALD layers, the thickness of each different layer (which is controlled by the number of cycles) and the chamber temperature, which may be varied in order to obtain amorphous or crystalline phases.

Some reviews of ALE/ALD techniques were already presented in the last decades, by Herman [1](1991), Lakomaa, et al. [2](1992), Niinistoo & Leskela, [3](1993), Ritala [4](1997), Niinisto [5](1998), Leskelä & Ritala [6](2003), George [7](2010), and mainly focused on the process parameters. Moreover, currently available reviews on this technique mainly considered optical and electronic applications. The aim of this review is to present an overview of the technique mainly focused on the potential implementations of ALD at an industrial level also considering different application areas other than electronic field.

To better understand all possible uses of industrial ALD processes, results from the literature are here revised along with new ones obtained on commercial substrates employed in different industrial fields, with a particular emphasis on corrosion protection.
Finally, this review is mainly consisted of a short historical overview of ALE/ALD techniques based in a time-line, a description of the principal ALD processes, a short list of applications and an overview on the most techniques used to characterize the different ALD coated substrates, and special attention to the discussion of corrosion results available in literature.

In order to give an idea about the historical evolution of the ALD-based processes for coating preparation a time-line of its development is presented in table 1. A totally equivalent technique to the modern ALD was first published under the name “Molecular Layering” in the early 1960’s by Prof. Kol’tsov (Sveshnikova and Kol’tsov, 1970 [8]; Aleskovskij, 1974 [9]; Suntola, 1989 [10] in Puurunen, 2005 [11]), under scientific supervision of Prof. Aleskovskij corresponding member of the Russian Academy of Sciences. This concept was used to produce structures of CdSe films evaporated on air-cleaved surfaces of sodium chloride, which were studied at various stages of the film growth by transmission electron microscope (Yasuda, 1968 [12]).

<table>
<thead>
<tr>
<th>Period</th>
<th>Technique/process</th>
<th>Development/property/application</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Switching effects in chalcogenide nanometric films</td>
<td>Suntola, 1971; Stubb et al., 1972; Suntola et al., 1972; Suntola, 1976.</td>
</tr>
<tr>
<td></td>
<td>ALD as an extension of ALE*</td>
<td>Solid state electronic devices.</td>
<td>Ahonen et al., 1976</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Amorphous semi-conductive thin films/semiconductors; Zinc telluride deposition on glass substrate: clean, smooth and featureless, and crystallized predominantly on (111) direction films were produced/crystal quality. Electronic structures remember the bulk materials ones.</td>
<td>Falck &amp; Jäntti, 1983; Tornqvist &amp; Korpela, 1982; Sutela, 1982.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wide-gap semi-magnetic semiconductors in Cd_{1-x}Mn_xTe; CdTe films with high structural perfection; Crystalline ZnS and amorphous ZnO films; ZnS/ZnTe and ZnSe/ZnTe superlattice films;GaAs, InAs and In,Ga_{1-x}As layers/ semiconductors.</td>
<td>Tammenmaa et al., 1986.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Doped ZnS films with rare earth β-diketonates/intense luminescence.</td>
<td></td>
</tr>
</tbody>
</table>

Table 16: Historical overview of ALD
**Part I - Chapter 3: Introduction to ALD**

ALD was introduced referring to ALE. ECALE technology is reviewed.

New materials deposited, also pure metals. Selective atomic decomposition of the precursors/improvement the yield of ALE technique. Single atomic layers deposited by “under-potential deposition”.

After this year: ALE when epitaxial structure is mainly focused; ALD when amorphous or crystalline structure is considered not fundamental.

Amorphous or crystalline TiO₂ deposits were obtained depending on temperature. Crystalline and amorphous Al₂O₃; substrate influence on ALE processes is recognized.

Optical properties: TiO₂/selective reflective membranes or light filters.

Corrosion studies: Al₂O₃ and TiO₂/stainless steel protection against corrosion.

### 2000's - ALD or ALE

| New applications for ALE: Fe₂O₃ onto Al nanoparticles/thermite materials; nanocomposite; barrier membranes; UV treated coatings/wettability control; encapsulation of organic solar cells, La₀.₈Sr₀.₂MnO₃ (LSM) cathodes/solid oxide fuel cells; deposition of Cu interconnections on ruthenium/ microelectronic application. |
| Simulation of precursors gases behavior during deposition and their molecular binding: effect of the substrate. |
| ALD with catalytic properties: V₂O₅, WOₓ, TiO₂, Pt/ conformally applied on porous membranes of alumina, silica or polymeric substrates. |
| ALD with optical properties: HfO₂, TiO₂, ZnO and Al₂O₃/ selective reflective membranes or light filters. |
| Nanometric layers: ZnO and InS for Cu(In,Ga)Se₂, boron-doped ZnO thin-films; HfO₂, Al₂O₃ and TiO₂ layers/solar cells. |

| Herman, 1991 |
| Aoyagi et al., 1991; |
| Gregory & Stickneyl, 1991 |
| Sanders & Kitai, 1992 |
| Lakomaa et al. 1992 |
| Lakomaa et al., 1996 |
| Aarik et al., 1997 |
| Matero, et al., 1999 |
| Fergurson et al., 2005; Liang et al., 2008; Kemell et al., 2008; Sarkar et al., 2010; Holme et al., 2008; Gebregziabiher et al., 2010. |
| Nielsen et al., 2001 PARTS I, II and III; Ahn et al., 2010; Gobbert et al., 2010. |
| Keranen et al., 2003; Herrera et al., 2006; Lee et al., 2009; Li et al., 2009. |
| Aarik et al., 2006; Kim et al., 2010; Aslan et al., 2010. |
| Yousfi et al., 2001; Naghavi et al., 2004; Yamamoto et al., 2001; Sang et al., 2001; Ganapathy et al., 2010; Shanmugam et al., 2010. |
Protective properties: protection of micro-electromechanical devices and nanodiamonds/against oxidation; wear and cavitation of metallic alloys.

The temperature of the substrate, at which oriented structures overgrowth occurred, was found to be about 130°C, being lower on step-rich regions than on step-free regions of the cleavage surface. This result was explained as the effect of the particles coalescence in the initial stage of growth.

The modern concept of ALD is an extension of the ALE, patented by Prof. Suntola (Suntola & Antson, 1977 [13]). Suntola’s studies were mainly focused on switching effects in chalcogenide nanometric films for solid state electronic devices (Suntola, 1971 [14]; Stubb et al., 1972 [15]; Suntola et al., 1972 [16]), and lately extended to a wide range of amorphous semi-conductive thin films (Suntola, 1976 [17]). Considering the deposited zinc telluride on a glass substrate by using “Atomic Layer Evaporation” technique (Ahonen et al., 1980 [18]), it was found to be clean, smooth and featureless, and crystallized preferentially with the orientation in the (111) direction. From the beginning, it was also observed that: “There seemed to be no narrow-range “optimum” temperature affecting the quality of the crystals when grown by using ALE process, in sharp contrast to the case in which the films were grown by codeposition of the elements”. The electronic structure of the films exhibited characteristic features of the bulk material, as deduced from the angle-resolved photoemission and optical absorption measures. In addition, some features which were supposed to be related to particular properties of the surface were present in the photoemission spectra. In 1980’s, the interest in ALE has known an exponential increase, mainly for the production of ZnS:Mn thin electroluminescent film on flat-panel displays, which required the production of high quality dielectric and luminescent films on substrates of large area (Falck & Jäntti, 1983 [19]; Tornqvist & Korpela, 1982 [20]; Sutela, 1982 [21]). Great effort was also dedicated to produce and characterize new ALE films, such as wide-gap semi-magnetic semiconductors in Cd1−xMnxTe (Herman et al., 1984 [22]), CdTe films with high structural perfection (Pessa et al., 1984 [23]), crystalline ZnS and amorphous ZnO films (Tammenmaa et al., 1985 [24]), ZnS/ZnTe and ZnSe/ZnTe superlattice films (Takeda et al., 1986 [25]), and GaAs, InAs and InxGa1−xAs layers (Tischler & Bedair, 1986 [26]). It was also demonstrated the possibility to dope ZnS films with rare earths β-diketonates using ALE processes, resulting in an intense luminescence (Tammenma et al. 1986 [27]).

The first twelve years of ALE technological developments and applications were reviewed (Herman, 1991 [1]). As ALE showed promising properties, the number of research contributions on this topic strongly increased, and new materials were deposited, in particular pure metals. Two widely used variations of the standard ALE technique were developed: 1) Laser Assisted ALE (Laser-ALE) (Aoyagi et al., 1991 [28]), in which a high energetic laser beam is used to obtain a selective atomic decomposition of the precursors, and 2) Electrochemical ALE (ECALE) (Gregory & Stickneyl, 1991 [29]), which is an under-potential deposition, and shares with ALE only the fact
that the films are deposited as a sequence of single atomic layers. To distinguish the conventional treatment from the new developed techniques, the term Thermal-ALE/ALD will be used from this point on. In 1992, the term ALD referring to ALE process was explicitly used (Sanders & Kitai, 1992 [30]). Since then, both acronyms were often used in slightly different acceptations: ALE when focusing on the epitaxial structure of the deposit and ALD when amorphous or crystalline structure is considered not fundamental. TiO$_2$ was successfully deposited using TiCl$_4$ and H$_2$O (Lakoma, et al., 1992 [2]) and it was shown that amorphous or crystalline TiO$_2$ can be obtained by ALE depending on the temperature inside the reaction chamber. Lately, crystalline and amorphous Al$_2$O$_3$ were successfully deposited using H$_2$O and Al(CH$_3$)$_3$ (Trimethylaluminum, TMA) (Lakomaa et al., 1996 [31]). AlCl$_3$ was not used because of the high temperature (around 500 °C) required to completely remove the residual chlorides. This work also showed that ALE processes depend on the substrate used.

In the last decade, investigations on ALD were mainly oriented to the research of new possible applications for ALD such as nanoparticles to produce enhanced thermite materials (Ferguson et al., 2005 [32]), La$_{0.8}$Sr$_{0.2}$MnO$_3$ (LSM) cathodes for solid oxide fuel cells (Holme et al., 2005 [33]), deposition of Cu interconnections on ruthenium for microelectronic application (Gebregziabiher et al., 2010 [34]), nanocomposite barrier membranes (Liang et al., 2008 [35]), UV treated coatings to control wettability (Kemell et al., 2008 [36]) and encapsulation of organic solar cells (Sarkar et al., 2010 [37]). Catalytic properties of different ALD coatings including metals and metallic oxides were also studied (Lee et al., 2009 [38], Li et al., 2009 [39], Keranen et al., 2003 [40], Herrera et al., 2006 [41]), and conformally applied on porous membranes of different chemical composition, for instance, alumina, silica or even polymeric substrates. Optical properties of ALD (Aarik et al., 2006 [42], Aarik et al., 1997 [43], Kim et al., 2010 [44], Aslan et al., 2010 [45]) were investigated in order to produce selective reflective membranes and light filters or to apply a coating without modifying the optical properties of the substrate. The intrinsic keen thickness and compositional controls offered by ALD have also shown promising results in the production of nanometric layers for solar cell applications (Yousfi et al., 2001 [46], Yamamoto et al., 2001 [47], Sang et al., 2001 [48], Naghavi et al., 2004 [49], Ganapathy et al., 2010 [50], Shanmugam et al., 2010 [51]. Driven by fundamental evolutions in electronics, informatics and computational sciences, important results were obtained in the last decade for the simulation of the behavior of precursor gases during deposition and their molecular binding in the presence of different substrates (Nielsen et al., 2001 PARTS I, II and III [52-54], Ahn et al., 2010 [55], Gobbert et al., 2010 [56]).

In 1999, the application of ALDs for corrosion protection of metallic substrates was considered for the first time (Matero et al., 1999 [57]). The protective properties of ALD oxide layers were also investigated at preliminary level, for the protection of micro-electromechanical devices (Hoivik et al., 2003 [58]; Tripp et al., 2006 [59]), nanodiamonds (Lu et al., 2007 [60]) against oxidation, magnesium alloys against wear and cavitation (Wang et al., 2010 [61]), stainless steel (Marin et al., 2011 [62], Díaz et al., 2011 [88]), and carbon steel (Díaz et al., 2011 [63]) against corrosion.
**ALD processes**

ALD (as ALE) process involves a sequence of self-limiting surface reactions. As evidenced for the first time in 1980 by Ahonen et al. [64], the self-limiting characteristic of each reaction step differentiates ALE and ALD from other chemical vapor deposition technologies.

![Figure 45: ALD process phases](image)

In ALD each deposition cycle is clearly divided in four steps (Fig. 45): in the first step a precursor is injected in the deposition chamber. The precursor is chosen so that its molecules will not react with each other at the deposition temperature. A single monolayer is thus formed as a result of the reaction with the substrate. In the second step, the chamber is purged with nitrogen or argon gas in order to remove the excess of reactant and prevent “parasitic” CVD deposition on the substrate, which will eventually occur if two different precursors are present in the deposition chamber at the same time. In the third step, the second precursor is injected in the chamber. In the case of metal oxide layers, this is an oxidant agent, usually simple H₂O. The last step of the deposition cycle is a second purge to remove the excess of reactant with purging gas.

Closed-loop repetitions of the four basic steps theoretically allow obtaining perfectly conformal deposits of any desired thickness. By avoiding the contact between the precursors throughout the whole coating process, a film growth at atomic layer control, with a thickness control within ~0.1 Å (10 pm), can be obtained.

Different types of ALE/ALD techniques were proposed in the last 20 years, combining different energy sources with gaseous or fluid precursors inside the deposition chamber:
Laser-ALE was first introduced in 1986 (Aoyagi et al. 1986 [65]) in order to grow GaAs layers. In their work, an enhanced growth rate by one or two orders of magnitude was observed due to the application of a laser source. This result could not be interpreted simply by the temperature increase on the irradiated area, and proved that the Ar+ laser irradiation triggers photochemical effects at the growing surface. Analysis of the carbon content showed that the laser irradiation enhances the decomposition of alkylgallium. The most noticeable difference in growth characteristics between thermal-ALE and laser-ALE resulted to be the source gases requirements as the Laser-ALE can be used to obtain reactions at lower temperatures compared to thermal-ALE. Laser-ALE also has advantages in direct writing of atomically controlled pattern defined epitaxial growth, thereby allowing maskless processing;

ECALE, proposed in 1991 (Gregory et al., 1991 [29]), involves the alternated electrochemical deposition of elements to form a compound. Epitaxial deposition is achieved by using under-potential deposition (UPD) to achieve surface chemistry-limited growth. UPD involves the deposition of one element on a second element at a potential lower than that required for the deposition of the first element on itself. Classically, UPD involves deposition of a less noble metal on a more noble metal. The driving force of UPD is the formation of a compound which is energetically favored relative to the bulk elements with a stoichiometry defined by the surface chemistry of the substrate. In the case of metals, a two-dimensional bimetallic compound is formed;

Liquid Phase ALE (LPALE) developed by Nicolau in 1985 [66]. LPALE was introduced as a successive ionic layer adsorption and reaction (SILAR) method. Analogous to the gas-phase ALE, the substrate is treated separately with each precursor followed by rinsing. The precursors are electrolytically dissolved in water and the rinsing agent is water. The process is controlled by the selective absorption of each ionic constituent and the effectiveness of the rinsing. The thickness of the adsorbed layer is limited to one ionic monolayer. The adsorption is affected by the type and the concentration of the ion, the pH of the precursor solution and the adsorption time which should be long enough to establish an equilibrium state between the hydrophilic diffusion layer and the liquid containing solvated precursor. The rinsing step is completed when the activity of the first component in the diffusion layer is low enough to avoid homogeneous precipitation during the subsequent immersion into the other precursor solution. The main advantages of LPALE technique are: ability to accurately control the film thickness by controlling the number of growth cycles, low costs and low temperature which allows using precursors susceptible to the temperature and the possibility to use substrates of large area;

Plasma Enhanced ALE (PEALE). The possibility of using Plasma for the activation of diatomic gases during ALE has been proposed for the first time in the early 1990’s (Niinistoo & Leskela, 1993 [66]). Nevertheless, research papers on plasma enhanced processes were not published until 2000 (Rossnagel et al., 2000 [67]), when H₂ plasma was used in order to deposit Ta using solid TaCl₅ powder as a precursor. The energy flux produced by the plasma gas inside the deposition chamber breaks the chemical bonds of the tantalum pentachloride, producing tantalum and HCl as reactants. It should be noticed that this is an efficient technique to produce pure metal layers without using high temperature processes. In similar ways it is also possible to
use oxygen or nitrogen instead of argon in order to produce oxide or nitride layers on the substrate;

- Modulated Ion Induced ALE (MIIALE) was patented by Chiang and Leeser in 2008 [68]. This technique was developed in order to solve problems related to Thermal-ALD, providing a non-thermal and non-pyrolytic means of triggering the deposition reaction. This technique enables the deposition of a pure film with high density at low temperature. The activation energy provided by a non-thermal source reduces the deposition temperature from 300-600 °C to about 25 °C. Modulating the ion flux and the energy of the ions striking the substrate the deposition reaction can be controlled precisely. Since the temperature is kept as low as possible, no significant reaction between the reactants and between the reactants and the substrate occurs until it is triggered by the ion beam;

- Photo-Assisted ALD (Photo-ALD) [Lee et al., 2004 [69]], in which an UV emitting lamp is used in order to facilitate the reaction between the two precursors, increasing the growth rate of the ALD layer and thus reducing the time required per each ALD cycle. Photo-ALD also proved to be effective in slightly reducing the temperature required to trigger the reaction between the two different precursors, effect that may be considered useful in particular when operating with low melting point alloys, like polymers or organic compounds.

Up to the present time, ALD processes have been successfully used to deposit several types of nanometric films, including several chemical compounds (e.g. AsGa, CdSe,...), metal oxides (e.g. Al₂O₃, CaO, CuO, Er₂O₃, Ga₂O₃, HfO₂, La₂O₃, MgO, Nb₂O₅, Sc₂O₃, SiO₂, Ta₂O₅, TiO₂, Y₂O₃, Yb₂O₅, ZnO, ZrO₂), nitrides (e.g. TiN, TaN, AlN, GaN, WN, NbN), sulfides (e.g. SrS, ZnS), carbides (e.g. TaC, TiC), fluorides (e.g. CaF₂, LaF₃, MgF₂), pure metals (e.g. Ru, Ir, Ta, Pt), biomaterials (e.g. hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂)) and even polymers (e.g. PMDA-DAH, PMDA-ODA) (Bedair, 1994 [70], Niinisto, 1998 [5], Ritala, 1997 [4]).
The ALD technique allows obtaining conformal coatings independent on the substrate with a theoretical coverage around 100% which can provide it special properties and protection.

SEMICONDUCTOR AND INSULATING FILMS

Historically, the production of polycrystalline ZnS:Mn$^{2+}$ and amorphous Al$_2$O$_3$ insulator films for electroluminescent flat panel displays has undoubtedly been the most important industrial application of the ALE process. In the mid 1990’s, rapidly increase the interest towards ALE has originated from the silicon-based microelectronics, in particular in consequence of the ever decreasing device dimensions and increasing aspect ratios in integrated circuits (IC) (Randall et al., 1996 [71]). Furthermore, the conformal thickness of ALE depositions has recently opened new possibilities for the production of nano-structured materials (Wade et al., 2001 [72]), diffusion barriers and components for nano-electronics (Aoyagi & Sugano, 1996 [73]). The application of ALE technique in the electronic field has been already extensively reviewed. Therefore, different application fields are considered in this review.

DIFFUSION BARRIER

Many ALD processes have been used in order to obtain a barrier effect against atoms or gases diffusion, in particular using depositions of oxides and nitrides. It has been shown by Lahtinen et al. (2011) [75] that Al$_2$O$_3$ ALD layers may be used to diminish the water vapor and oxygen transfer rate on polymer coated paper. Besling et al. (2004) [76] tested the barrier properties of TaN layers obtained by ALD in a HF solution and confronted them with those obtained by different physical vapor depositions techniques. The results evidenced that ALD films have greater barrier properties with respect to the PVD coatings and are more conformal to the substrate morphology. Xie et al. (2008) [78] showed a clear correlation between deposition parameters and barrier effect for TaN, films obtained by PE-ALD, in particular the plasma gas (N$_2$ or NH$_3$), the plasma exposure time or the reactant pressure. Kääriäinen et al. (2011) [79] & Kim et al. [80] observed that the barrier properties of ALD seem to be a function of the coating thickness, even if overall coating thickness could not be increased over 100 nm without triggering cracks. The cracks are developed due to residual coating stresses and, therefore, the barrier properties are reduced. Tantalum oxide was used by Lintanf-Salaun et al. (2011) [81] in order to prevent the thermal diffusion of copper in microelectronic devices and showed a good diffusion resistance up to the crystallization temperature of the coating (around 700 °C). This was supposed to be caused by the diffusion along the grain boundaries formed during crystallization. As observed by, Elers (2005) [82], not all effective ALD diffusion barriers can be conformally applied to any substrate due to the chemical compatibility.
Summarizing, ALD coatings seem to have promising barrier effects against gas diffusion, liquid diffusion and even solid thermal diffusion. The barrier effect resulted to be dependent on the specific deposition parameters, the chosen precursors, the exercise temperature and chemical composition of the final layer. For these reasons ALD diffusion barriers must be selected based on the specific application.

**Wear resistance**

Only preliminary wear resistance investigations have been carried out for ALD coated systems. As evidenced by Marin et al. (2009) [83] thin ALD layers cannot be an efficient way to reduce wear in processes involving high contact pressures. In this work, TiCN and TiAIN PVD deposits were applied on AISI M2 tool steel and then coated with a final layer of Al2O3 obtained by ALD. No wear decreasing was observed, while the TiCN coated sample showed a sensible increase in the friction coefficient. In addition, amorphous ceramic ALD layers cannot be useful in wear reduction, since the absence of a crystalline structure strongly reduces the hardness of a ceramic material and therefore is subjected to higher wear. Nevertheless, promising results were shown by Wang et al. (2011) [84] on Mg-Li alloys using an amorphous Al2O3 ALD coating for the reduction of cavitation wear, under low load conditions. The system showed a clear reduction in the friction coefficient compared to the bare alloy that might cause a wear reduction.

Further investigations of the tribological behavior of ALD coatings are needed in order to determine if ALD can really be effective in wear protection. The major bottleneck seems related to the ability to deposit hard crystalline coatings of carbides and nitrides, which can be expected to improve the wear resistance of the ALD films.

**Corrosion resistance**

Taking into account their nanometric thickness and their chemical composition, ALD oxide coatings may be considered an artificial imitation of spontaneously formed oxide layers that can be found on the surface of different metals and metallic alloys and in particular Titanium and Tantalum, well known for their excellent corrosion protection in most aggressive media (Shoesmith & Noël, 2010 [85], Lyon, 2010 [86]).

It is very interesting to note that corrosion studies of coatings prepared by ALD-based technologies using electrochemical techniques are recent and the major part of these studies are on coatings obtained by the Thermal-ALD technology; only three of them are dedicated to coatings prepared by PVD + ALD (Shan et al., 2008 [87], Marin et al., 2011 [62]) and PE-ALE (Díaz et al., 2011 [88], Potts et al., 2011 [89]). In the last decade, a number of researches were conducted on the potential use of ALD for the corrosion protection of different metal alloys mainly using salt spray tests and/or potentiodynamic polarization and electrochemical
impedance spectroscopy (EIS) techniques in aggressive solutions. From the vast number of chemical compounds, metallic oxides, nitrides, carbides, fluorides, sulfides, pure metals, biomaterials and even polymers deposited via ALD technologies (Bedair, 1994 [70], Niinisto, 1998 [5], Ritala, 1997 [4]), only for a few number of them such as Al$_2$O$_3$, TiO$_2$, Ta$_2$O$_5$, LiAl$_x$O$_y$ layers, Al$_2$O$_3$/TiO$_2$ the corrosion performance was evaluated, probably due to the fact that these oxides are naturally grown on the respective metal surfaces developing a passive layer.

Among the properties offered by ALD coatings some of them are very important to protect the substrate against corrosion in aggressive medium, such as compactness leading to low porosity even applying a nanometric film, low chemical reactivity, and conformability, which give to the ALD many advantages when compared to other technologies. However, the low adhesion to the substrate (poor mechanical and chemical interaction between ALD coating and substrate) and defects generated during the coating deposition are, probably, the main responsible for the low long term corrosion performance of the coatings prepared using ALD technologies.

Therefore, even if the corrosion resistance given by ALD coatings has a similar effect if compared to the protection given by the naturally formed oxide superficial layers, the growth process of the two layers is completely different and thus other properties of natural oxides are not offered by the ALD, such as:

- adhesion between coating and substrate, which in highly corrosion resistant alloys is given by the chemical affinity and the high stability of the metallic oxide in aqueous media;

- ability to “repassivate” in the presence of even low O$_2$ concentrations (Shoesmith et al., 2010 [85]).
ALD CHARACTERIZATION

THICKNESS AND MORPHOLOGY

Ideally, the ALD film thickness could be easily monitored, as it results from a self-controlled growth process in which the film thickness is only dependent on the number of repeated deposition cycles (Riihela et al., 1996 [90]). Actually, thickness control is required after the ALD in order to verify that the process has been performed correctly. Un-optimized chamber geometry, low vacuum, insufficient pressure of precursors, residual precursors, residual gases in the deposition chamber and rough control on the chamber temperature may drastically affect the real thickness of the ALD deposits even leading to not complete substrates coverage. Also, surface sample cleaning and chemical affinity with the precursors may cause localized or even diffused defects on the surface.

During deposition, few techniques can be successfully used to monitor precursors and residual gases and therefore to obtain preliminary information about the deposition. These techniques include Spectroscopic Ellipsometry (Langereis et al., 2009 [91]), Optical Emission Spectroscopy, Mass Spectrometry and Infrared Spectroscopy (Niinisto, 1998 [4]).

After deposition, ALD layer thickness can be measured using a wide array of techniques:

- Indirect techniques: reflectance anisotropy spectroscopy (RAS) (Patrikarakos et al., 1997 [92]), reflectance difference spectroscopy (RDS) (Arinaga & Tanaka, 1994 [93]), surface photo-absorption (SPA) (Simko et al., 1993 [94]), Resonance Raman (Gichuhi et al., 2002 [95]), spectroscopic ellipsometry (Mitchell et al., 2005 [96]), Fourier-transform infrared (FTIR) Spectroscopy (Wu et al., 1996 [97]), Grazing Incidence X-ray Reflectivity (XRR) (Ferrari et al., 2004 [98]), Glow Discharge Optical Emission Spectrometry (GDOES) (Marin et al., 2009), Gravimetry (Koukitu et al., 1997 [99])

- Contact techniques: High Resolution Profilometer (Figure 2), Scanning Tunneling Microscopy (STM) (Miwa et al., 1996 [100]), Atomic Force Microscope (AFM) (Ihanus et al., 1997 [101]) (Figure 3). Figure 46 shows the profile obtained using a contact profilometer at the coated/uncoated interface of a silicon wafer sample coated with about 100 nm of TiO$_2$ obtained by Thermal-ALD, with a vertical resolution of about 2 nm. This measure is very simple and fast and gives reliable data if a smooth substrate surface is used as shown above. Figure 47 shows the topographical AFM map of a coated/uncoated interface of a stainless steel sample coated with about 100 nm of TiO$_2$, and vertical resolution of about 0.2 nm. This technique presents higher resolution, generally at smaller areas, requires more time to get the data and is much more expensive;
- Microscopy techniques: Transmission Electron Microscope (TEM) (Gluch et al., 2010 [102]), Scanning Electron Microscope (SEM) (Figure 48), Focused Ion Beam (FIB) (Leskela et al., 2003 [6]). Figure 4 shows the SEM cross-section of a 100 nm TiO$_2$ Thermal-ALD coating applied on a 1 μm layer of Silver obtained by Ion Beam Assisted Deposition (IBAD). As can be seen, it is very important the sample surface preparation, which means to obtain a clear fracture without damage to the coating;

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Since nanometric ALD coatings may have a thickness close to resolution limit for some of these techniques, it is common practice to combine two or more of them, based on different principles in order to obtain complementary information.

**COMPOSITION AND STRUCTURE**

The number of compositional analytical techniques that can be successfully used on ALD layers is strongly limited due to the nanometric thickness of the coatings. As a matter of fact, a large number of analytical techniques, such as common SEM Energy Dispersive X-ray Spectroscopy (SEM-EDXS), require thicker layers in order to give a reliable compositional analysis. The most common techniques to evaluate the composition of ALD actually present in literature are:

- **Crystallographic structure based:** X-ray photoelectron diffraction (XPD) (Cecconi et al., 2001) [Varazo et al., 2002 [104]], X-ray photoelectron spectroscopy (XPS) (Diaz et al., 2011 [63]), Raman (Gichuhi et al., 2002 [95]), Reflection High Energy Electron Diffraction (RHEED) (Akihiro et al., 1999 [105]), Total-Reflection-Angle X-ray Spectroscopy (TRAXS) (Akihiro et al., 1999 [105]), Low Energy Electron Diffraction (LEED) (Varazo et al., 2002 [104]), Photoluminescence (PL) (Hsu, 1999 [106]), X-Ray Absorption Near Edge Structure (XANES) (Deng et al., 2011 [107]), Extended X-Ray Absorption Fine Structure (EXAFS) (Loglio et al., 2005 [108]);

- **Crystallographic structure independent:** Glow Discharge Optical Emission Spectrometry (GDOES) (Marin et al., 2009 [83]). In fig. 49a-c GDOES results are shown for ALD mono-bi-and multilayers. GDOES technique gives information about the in depth compositional profile of the
coatings with a nanometric depth resolution. The principal drawbacks of the technique include
the necessity to perform a specific, keen calibration for each element and the scattering caused
by the surface roughness, which results in not sharp interfaces between different layers. Other
techniques include Secondary ion mass spectrometry (SIMS) (Diaz et al., 2011 [88]), TEM Energy
Dispersive X-Ray Spectrometry (EDS) (Mitchell et al., 2005 [96]);

Not all the techniques used for the compositional analysis can be applied to obtain the same
information on ALD coating: in fact, Crystallographic Structure Based techniques will need not-
amorphous layers but will also give useful information about the crystallographic structure of
the coating; some techniques will give in depth profiles, while other techniques will give only
overall compositional data.

As a matter of fact, depending on the specific application of the coating, different techniques
may be in fact needed to obtain a complete characterization of ALD.

**ADHESION AND WEAR**

Adhesion and wear information about ALD coatings have been obtained using different
techniques, mainly with a comparative approach. Triani et al. (2010) [110], for example,
 obtained delamination resistance data from optical observations of coated samples under
tensile stress. Kemell et al. (2008) [111] used a Scotch tape test, in which scotch tape is pressed against the surface and removed, and then the coating damage is evaluated. Lahtinen et al. (2011) [112], investigating extrusion-polymer coated papers protected with ALD, obtained information about the adhesion of the coating by determining the extent of fiber tear when drawn. Other research groups, such as Latella et al. (2007) [113] evaluated the adhesion from fracture mechanics calculations. Adhesion evaluations can also be obtained by mechanically damaging of the surface of the coated samples, for example by an indentation (Fig. 50) or a scratch and then calculating forces and binding energies. Interesting results about binding energies were obtained by Ding et al. (2007) [114] using micro-scratches. Even if the scratch morphology was found apparently different at every measurement, the binding energy evaluation resulted to be quite reliable and thus provided adhesion values of Al₂O₃ layers on Si, SiO₂ and polyimide substrates.

For future industrial applications, a standardized, universal evaluation method for the binding energy of ALD on the substrate will be necessary in order to compare different ALD technologies.

**Corrosion resistance**

The corrosion resistance given by ALD processes has been mainly evaluated using two different electrochemical techniques: Electrochemical Impedance Spectroscopy (EIS) and Potentiodynamic Polarization (PP). In all cases, due to the tendency of ALD to have a time limited effect (Matero, 1999) [57], EIS analysis could be not carried out for long immersion times.
and only gave preliminary information about the behaviour of the coating after few minutes or hours of immersion in an aggressive solution. Up to now, an investigative experimental setting about the corrosion resistance of ALD deposits as a function of the immersion time in aggressive media has not been considered in literature.

Matero et al. (1999) [57] considered for the first time that the flawless coverage of the substrate obtained by the application of ALDs could be used for corrosion protection of metallic substrates, in particular stainless steel. Preliminary results obtained using Al₂O₃ and TiO₂ deposited at different temperatures showed a “time limited” protection of the steel substrate in naturally aerated 0.1 M NaCl environment, while Ta₂O₅ layers showed some extent of protection even in diluted HCl solutions.

Shan et al. (2007, 2008) [87,116] showed preliminary data above 50 nm thick ALD titanium dioxide film obtained from Titanium tetraisopropoxide (TTIP: Ti[OCH(CH₃)₂]₄) and water. The coating was applied on Stainless Steel and CrN coated stainless steel in order to further increase the corrosion resistance. In the case that the two coatings were present, the CrN coating was amorphous while TiO₂ was deposit in the crystalline anatase structure and covered possible cracks and pinholes of CrN coating. In both cases potentiodynamic polarization curves have been obtained in a 3%wt. NaCl solution. The corrosion current density decreased from 2.6 * 10⁻⁶ to 1.9*10⁻⁶ and to 0.31*10⁻⁶ A/cm² respectively, for stainless steel (SS), CrN/SS and TiO₂/CrN/SS, even if the results have been probably influenced by the high scan rate used (v= 10 mV/s). It was also observed an increase of the corrosion potential (V/SCE): SS (-0.95 V), CrN/SS (-0.74 V) and TiO₂/CrN/SS (-0.49 V). Both corrosion current density and corrosion potential indicated an increase of corrosion resistance when the ALD layer was applied. Nevertheless, the authors observed that ALD deposition may be used to further improve the efficiency of other protective films, closing residual porosities and pinholes. These experimental observations seem to find confirmation in the experimental setting carried out by Marin et al. (2009) [83] on PVD coated tool steel components. In fact, it is well-known that the most of commercial PVD coatings cannot offer a very good corrosion protection due to some defects and pinholes present in the layer. TiO₂-based coatings, depending on the medium, can be dissolved and then they do not play an important role in blocking pinholes and cracks, however if the medium is not so aggressive, like sodium chloride in neutral solution the TiO₂ layer improves the corrosion resistance of CrN/SS. The corrosion resistance of the TiO₂ coating was confirmed with EIS measurements (Shan, et al. 2008 [87]).

In general electrochemical techniques have been used to estimate the porosity due to pinholes and defects (Tato and Landolt, 1998 [117]) in several coatings prepared by ALD/ALE-based technologies (Díaz et al., 2011, Diaz, et al., 2011 [87-116], Potts et al., 2011 [89]). Depending on the substrate very high porosity values (until around 50%) were measured using electrochemical technique (Potts et al., 2011 [89]), as mentioned by the authors this value is unrealistic high to be considered as porosity. However, it must be mentioned that it is very difficult to get reliable porosity data by means of an indirect measurement without comparison with, for instance, a microscopy evaluation. Since, an estimative of porosity of these coatings had proved to be very
difficult using SEM or even AFM due to the dimension of residual porosity and defects, another technique should be used or developed.

ALD was applied in order to seal residual porosities of the PVD coating and thus to enhance corrosion protection (Marin et al., 2009 [83]). Even if tool steel is drastically prone to pitting corrosion, the application of combined PVD + ALD coating diminished the corrosion current density from $10^{-5}$ A/cm$^2$ for a tool steel to $10^{-6}$ A/cm$^2$ for a PVD coating applied on tool steel and to $10^{-7}$ A/cm$^2$ when an ALD layer was applied on the PVD coating. Another parameter that indicates the improvement of the material protection by ALD is the potential range of the passive region, which is 0.6 V (from -0.3 to 0.3 V/AgqAgCl/KCl3M), while practically no passive region was observed for the other systems here investigated. ALD layer was also effective to protect the TiCN coating against corrosion for short immersion times (some hours). In this case, the passive region (around 150 mV) was also only observed after applying the Thermal-ALD coating and the corrosion current density decreased to $10^{-7}$ A/cm$^2$. This work was complemented by GDOES (Glow Discharge Optical Emission Spectrometry) analysis which allows getting information on the in-depth composition of the coatings. The results show an oxygen-enriched surface which was attributed to an artefact; however it was detected along the whole thickness of the TiCN coating and not on the surface only.

Similar depositions were carried out following a different approach by Wang et al. (2010) [84]. In their work, a conventional ALD coating based on TMA and H$_2$O was applied on a magnesium-lithium alloy substrate at 200 °C. In this case, the aim of the deposition was to form LiAl$_2$O$_3$ layers on the surface of the sample, promoting the lithium diffusion from the substrate to the coating/substrate interface and thus increasing the adhesion between coating and substrate. The polarization curves for bare LZ101 alloy and covered with ALD-deposited LiAl$_2$O$_3$ films of various thicknesses (65, 130 and 200 nm) surprisingly did not present any passive potential range, only a significant positive shifting in the corrosion potential (around 0.5 V) along with a decrease of the corrosion current density in about one order of magnitude when the bare electrode received the thicker Thermal-ALD coating. The same coatings were also evaluated in respect to wear and cavitation-erosion (Wang et al., 2010 [61]). The authors considered positive the improvement of wear performance and erosion resistance presented by the Thermal-ALD coatings.

Other results from Marin et al. (2011) [62] on pickled and skinpassed (steel which has been processed through the Skin Mill or Temper Mill) AISI 316 stainless steel sheets coated with a relatively thick Al$_2$O$_3$/TiO$_2$ ALD bi-layer (80 nm of Al$_2$O$_3$ and 200 nm of TiO$_2$) clearly showed no significant effect of the ALD deposition on the substrate morphology and roughness. However, it is to be noted that the GDOES analysis showed that the bi-layer coating showed and intermixed region which favors continuity and adhesion between layers. Polarization curves recorded in 0.2 M NaCl aqueous solution showed a decrease of corrosion current density after depositing the Thermal-ALD coating of at least 2 orders of magnitude reaching a so low value as $10^{-9}$ A/cm$^2$. These results clearly indicate the benefit to the substrate protection against corrosion due to the TiO$2$/A2O3 ALD coatings.
Furthermore, Diaz et al. (2011) [63], studying stainless steels corrosion protection by Al2O3 ALD layers clearly showed that the ALD protective effect is strictly correlated to the thickness of the deposited layer, as even controlled ALD processes are prone to defectivity, usually due to unreacted precursors and/or contaminations. The residual porosity seemed to be inversely proportional to the coating thickness and as low as 0.01% for a 100 nm coating. However, only a slight shifting towards nobler corrosion potentials was observed after applying the Al2O3 coating by Thermal-ALD technology, while according to the authors the corrosion current density decreased by about four orders of magnitude (the lowest corrosion current density near $10^{-10}$ A/cm$^2$) for the coating 100 nm thick compared to the bare SS. The high corrosion resistance was also measured using EIS and the results were interpreted based on one equivalent circuit with only one time constant. The authors considered that for lower coating thicknesses the electrical double layer predominates and at high sealing properties the coating capacitance became dominant, and the pore resistance was considered negligible when compared with the charge transfer one due to the nanometers range of the thin coatings; charge transfer resistance of about $5 \times 10^8$ Ω were obtained (geometric area of the electrode: 0.44 cm$^2$). The values of capacitance of the coating was around $10^8$ F and the CPE power value was similar to the substrate for the 10 nm thick layer ($n=0.86$) while this value was 0.95 and 0.99 for the 50 and 100 nm thick layers, respectively, indicating that some roughness present on the substrate and the very thin layer diminishes significantly as the coating thickness increases. Similar electrochemical study was developed for ultra-thin (from 5 to 50 nm) Al2O3 and Ta2O5 coatings deposited by Thermal-ALD on SS (Díaz, et al., 2011, [63]), in 0.8 M NaCl solution. The passive current density values were always below $10^{-7}$ A/cm$^2$ reaching $10^{-10}$ A/cm$^2$, practically the limit of the measuring instrument (as can be deduced from the polarization curves published), for the coatings prepared at 250 °C. Also the real impedance values for aluminium oxide coating deposited by ALD at 250 °C were around $10^{-9}$ Ω, confirming the high corrosion resistance of the coatings prepared by ALD-based technologies.

Potts et al. (2011) [89] also studied ultra-thin (10-50 nm) aluminum oxides films, now deposited by PE-ALE, for corrosion protection of 100Cr6 steel and Al2024-T3 alloys. Considering corrosion subject in this work only salt-spray tests were done it was observed that all coatings studied were degraded after 4 hours, and some of them even after 2 hours, as a clear indication that the main drawback of this technology is the time limited corrosion protection.

Polarization curves performed in aggressive media clearly showed that the protection given by the Thermal-ALD layers might be comparable or even superior to the one obtained with conventional, means thicker coatings. Thermal-ALD coated substrates often showed a sensible decrease in the corrosion current density and wider passive potential regions if compared with uncoated substrates. In Thermal-ALD coatings, corrosion protection seems to be influenced by both overall coating thickness and number of different layers applied (Marin et al., 2011).
Figure 51 shows polarization curves obtained for different alloys before and after the application of a 100 nm ALD coating which was obtained by four alternate Al$_2$O$_3$ and TiO$_2$ layers (chamber temperature: 120 °C precursors: TMA, TiCl$_4$ and H$_2$O. All polarization curves were recorded in naturally aerated and unstirred 0.2 M NaCl solution at 0.2 mV/s. Both martensitic (AISI 420, Fig.
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Chapter 3: Introduction to ALD

51(a)) and austenitic (AISI 316, Fig. 51(b)) stainless steels showed a sensible reduction of the corrosion current density, from about $10^{-7}$ to about $10^{-10}$ A/cm$^2$ and the presence of a wide well defined passive region (from ... to ... potential region), which is sensibly wider than the passive region previously shown by the uncoated alloys (from ... to ... potential region). In the case of cobalt alloys (Fig. 51(c)), corrosion current density decreased from about $10^{-7}$ to about $10^{-10}$ A/cm$^2$, while the already present passive region resulted to be better defined after deposition, with almost constant current density from -0.2 V to about 0.8 V vs. Ag/AgCl/3 M KCl. In the case of 2024 aluminum alloy, Fig. 51(d), the application of ALD decreased the corrosion current density from about $10^{-5}$ to about $10^{-9}$ A/cm$^2$ in a naturally aerated and unstirred 0.05 M NaCl solution. In the polarization curve of 2024 aluminum alloy as expected no passive region was observed, while for the ALD coating the barrier effect was present as observed by a small potential region (about 0.04 V) with low and almost constant current density.

In the case of magnesium ASTM AZ31 (Fig. 51(e)), the application of ALD diminished the corrosion current density from about $10^{-4}$ to about $10^{-8}$ A/cm$^2$ and the corrosion potential was less noble than magnesium-based alloy, suggesting that the substrate presents higher activity at the bottom of the pores. The ALD deposits (100 nm thick) present residual nanometric pores and considering the small thickness of the ALD deposits it is possible that the electrolyte penetrates the pores and reaches the substrate. Therefore, an ohmic behavior can be expected where the current is controlled by the resistance of the solution inside the pores for thicker layers. In fact, for the thick layers, if the polarization curve is given as I-E plot a linear straight line is obtained as shown in the inset in Fig. 51e.

The strong corrosion current density decreasing obtained for Al2024 and Mg AZ-31 is considered a promising result for the industrial application of Thermal-ALD as a barrier layer for corrosion protection, since no other nanometric treatments actually investigated in literature could give similar properties. Both Sterling Silver (Fig. 51(f)) and commercially pure copper (Fig. 51(g)) were tested in a 0.2 M NaCl solution in which 600 mg of CuS were added in order to promote surface tarnishing. For uncoated samples, generalized tarnishing phenomena were optically observed on the whole area after testing. In both cases, after the application of ALD deposit, a corrosion current density reduction from $10^{-4}$ to about $10^{-6}$ A/cm$^2$ for Sterling Silver and from about $10^{-6}$ to about $2\times10^{-7}$ A/cm$^2$ for commercially pure copper was observed. Only in the case of Sterling Silver the appearance of an extended potential range of about 0.5 V with low current density was observed, indicating a better barrier layer performance. After testing both samples showed localized tarnishing phenomena on the surface, probably in concomitance with localized defects of the protective layer.

As can be deduced from Fig. 51, the protective effect of Thermal-ALD deposition is not strictly related to the nature and chemical composition of the substrate or on the chemical affinity between the substrate and the coating, but mainly related to a barrier effect. In conclusion the protection offered by these conformal nanometric coatings seems to be superior or at least comparable to conventional industrial coatings.

As demonstrated by Shan et al. (2008) [87] and Marin et al. (2009) [83] Thermal-ALD can also be successfully combined with other deposition techniques in order to obtain a more protective
coating due to the pore-sealing effect shown by the conformal ALD coating. This effect is not limited to PVD coatings, because similar results can be obtained by Thermal-ALD deposition on sol-gel coatings (Fig. 52).

![Figure 52: Polarization curves for Al2024, Al2024 coated with Zr based sol-gel coating and Al2024 coated with sol-gel coating and an Al2O3 ALD layer.](image)

The protective effect given by ZrO2 sol-gel coatings has been explored in literature (Andretta, 2007 [118]; Andreatta 2011 [119]). The application on aluminum alloys of compact and adherent sol-gel coatings allows obtaining a corrosion current density decreasing from $10^{-5}$ to about $10^{-8}$ A/cm$^2$. This parameter can be further decreased down to $10^{-11}$ A/cm$^2$ by the subsequent deposition of a 50 nm layer of Al$_2$O$_3$ which was obtained by Thermal-ALD, which means at least 5 orders of magnitude below the substrate. Combined deposition techniques with Thermal-ALD top layers are probably the most promising applications for this technology in the field of corrosion protection, even if further results and investigations are required in order to fully understand the possible interaction between the different coatings and the long term efficiency of these systems.
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Chapter 4: Aim of the Work

4 - AIM OF THE WORK

OBJECTIVE

The protective capabilities of ALD applied on biomedical alloys and in particular on AISI 316 L stainless steel have been deeply investigated on this part of the work, with the main objective of developing thin ALD protective layers that may be applied on biomedical stainless steels in order to enhance their naturally high corrosion resistance in aggressive biological medias.

The second objective of the experimental setting was to obtain suitable protective ALD coatings with reduced deposition times in order to greatly reduce the overall process costs and greatly improve the productivity of the ALD implant. Using a deposition chamber of about 1.0 m$^3$ it can be estimated that ALD processes based on TiO$_2$ and Al$_2$O$_3$ have a duration of about 6h per 100 nm of deposited materials plus about two hours for the substrate preparation, the chamber loading and the chamber unloading, with a total process cost of about 2000 € for each deposition cycle and a maximum of three depositions per day, resulting in a very expensive technique. As coating costs shall not exceed 10% of the entire cost of the component, 100 nm ALD processes seem to be profitable only for protection of components of high value. For this reason, configurations down to 10 nm (approximate cost: 380 € per deposition process) were tested.

PREVIOUS BIOMEDICAL APPLICATIONS FROM LITERATURE

Even if ALD allows to deposit a wide array a bio-compatible or bio-inert materials, such as metallic oxides and nitrides of Titanium and Aluminum, only few research papers are actually present on the possibility to use ALD layers in biological environments.

One possible biologically-related application of ALD is for the chemical protection of packaging materials for food and drug delivery. ALD in fact has recently been effectively used to enhance the water vapour barrier characteristics of PEM coated Polylactide (PLA) films, thanks to an increase in the hydrophobicity of these films. PLA is the most used base material for bio-based packaging materials currently in the marked, thanks to its sustainability, recyclability and biodegradability [1]. However, the sensitivity of biopolymers towards moisture has restricted its used. To overcome the problem, various surface treatment approaches have been considered to enhance the water vapour barrier properties of biopolymers. A simple and cost-effective way to functionalize bio-polymer surfaces is to coat them with a polyelectrolyte multilayer (PEM) film [2-5]. Water vapour barrier properties were considerably improved after employing a PEM + Al$_2$O$_3$ ALD double coatings. Most importantly, the properties were improved more than by applying just the PEM or the Al$_2$O$_3$ coating [6].
But the high versatility of ALD technology can be also used in order to obtain nanofabricated surfaces to be used on nano-biodevices and nano-biomaterials. In 2009, Kim et al. [7] reviewed a substantial list of ALD applications actually in research, mainly oriented on the surface modification of nanometric biological devices. The possibility to produce nanowires and nanotubes (1D) or nanodots (0D) is in fact considered as essential building blocks for the realization of nanotechnology [8-9], and ALD is a promising technique to be used to produce such components. The ability to deposit films at low growth temperature, in particular, is very attractive for polymer based devices and for coating heat-sensitive materials such as polymers and biomaterials [10-11]. ALD has been identified as an ideal technique to form protective coatings on nanowires [12] and nanorods [13]. This ability has then been fully exploited in the production of biotemplating components. Biotemplating is attracting great interests [14] as a new way of bottom up fabrication of nanomaterials. By biotemplating, complex shaped nanomaterials can be relatively easily constructed by replicating the morphology or shape of naturally existing materials without complicated sintering methods. For example, ALD on tobacco mosaic virus (TMV) was reported by a research group at the Max Planck Institute [15]. TiO$_2$ and Al$_2$O$_3$ films were conformally deposited on top of dispersed TMVs on substrates, resulting in hollow oxide nanotube formation. Free standing metal oxide films with embedded ferritin molecules were also obtained. The replication of larger scale biospecies was reported recently. ALD of Al$_2$O$_3$ was applied to replicate the wing of a butterfly and the eye of a household fly [16,17]. ALD is also used to make porous nanocomposite materials by coating of nanoporous materials such as aerogels. Aerogels are materials with nanoscale size pores, which are made through wet chemistry [18], with potential applications including biosensors and batteries.

ALD can also be used in order to functionalize the surface of biomaterials for implanting. The most studied functional coating in this field is hydroxyapatite. In literature, hydroxyapatite coatings have been successfully deposited on Si(100) and Corning (0211) using Ca(thd)$_2$, where thd is 2,2,6,6-tetramethyl-3,5-heptanedionato and (CH$_3$)$_3$PO[19]. Previously Ca(thd)$_2$ has been used for the ALD deposition of calcium containing films, such as CaO [20,21], CaS [22-25] and CaF [26]. Rapid thermal annealing was carried out using a PEO 601 system in N$_2$ and O$_2$ atmospheres (>99,999%) at 400-1000 °C. Typical annealing times were 10-20 min. Dry annealing was carried out in an RTA oven with the heating rate of 25-35 °C/min. The as-deposited and annealed Ca-P-O films were then analysed and, finally, MC3T3-E1 mouse cell culture on experiments were carried on sterilized samples. The thermal annealing proved to be a good method to reduce the carbonate content and form hydroxide groups in the film. During the cell culture experiments, after only 3 hours of annealing osteoblasts have formed lamellipodia rich in actin bundles extend from the leading edges of the cells.

Due to its chemical stability, uniform pore size and high pore density, nanoporous alumina is being investigated for use in biosensing, drug delivery, hemodialysis and other medical applications. In recent work, the use of ALD for coating the surface of nanoporous alumina membranes has been studied. Zinc oxide-coated alumina membranes demonstrated antimicrobial activity against Escherichia Coli and Staphylococcus Aureus bacteria [27] and an increased proliferation of cells due to an activation of mitogen activated protein kinase and promotion of DNA synthesis by zinc [28,29], suggesting that atomic layer deposition may be an
attractive technique for modifying the surfaces of nanoporous alumina membranes and other nanostructured biomaterials. In particular, as stated by Xiong et al. [30] and Adiga et al. [31], ALD may be used to prevent release of impurities and to decrease the size of the pores within nanoporous alumina membranes in a controlled manner.

Up until now, no scientific effort was made to investigate the suitability of ALD for the corrosion protection of metal alloys in biological environments.
REFERENCES


5 - SAMPLES PREPARATION

As a substrate for deposition, AISI 316 L stainless steel sheets were obtained by cold rolling. In the first experimental setting, cold rolled and pickled substrates’ results were compared with cold rolled, pickled and skinpassed ones, in order to understand the influence of the substrate roughness and morphology on ALD properties such as delamination and corrosion resistance (Figure 53).

![Figure 53: Substrate preparation for the first experimental campaign, cold rolling, pickling and skinpassing](image)

From the second experimental setting on, substrates were cold rolled, pickled, skinpassed and then polished till a surface roughness of about 20 nm Ra was obtained (Figure 54). This procedure was chosen in order to obtain reliable results, in particular with high resolution techniques such as GDOES and AFM which required a particularly good surface finishing.

![Figure 54: Additional substrate preparation for the following experimental campaign, cutting, polishing, cleaning in ultrasonic bath and coating](image)

After preparation, the AISI 316 L substrates were deposited with a list of different ALD-based Al₂O₃ and TiO₂ strategies, in order to better understand the mechanical and electrochemical behavior of the different layers. The aim of these experimental settings was to find a way to obtain protective ALD coatings with low thickness and deposition time, in order to optimize the cost/performance ratio.
FIRST EXPERIMENTAL SETTING

In order to verify the corrosion protection offered to AISI 316 L by the application of ALD coatings and verify the influence of the substrate roughness, for the first experimental setting a standard ALD treatment composed of about 80 nm of Al₂O₃ followed by 200 nm of TiO₂, both deposited at 120°C, was chosen. This coating configuration was proposed by the producer of the ALD deposition system, Beneq Oy. The coating configuration is shown on Figure 55. To aid optical comparison, from Figure 55 to 59 all coating thickness in pixels are proportional to the real values in nanometers.

![Figure 55: Coating configuration for the first experimental setting](image)

SECOND EXPERIMENTAL SETTING

As the surface roughness showed really low influence on the corrosion protection offered to AISI 316 L Stainless Steel by ALD, other experimental settings were performed only on polished surfaces. Due to the long deposition time required in order to deposit a 280 nm coating (about 24 hours), to reduce the deposition costs new configurations of about 100 nm were investigated (deposition time: about 8 hours). To discriminate the behavior of TiO₂ and Al₂O₃, single layer of TiO₂ (A) and Al₂O₃ (B) presented in Figures 56a & 56b as well as two simple multilayer configurations, based on two (C) and four (D) alternate layers were tested (Figures 56c & 56d).
As multilayer configurations are well known from literature for improving the corrosion resistance compared to single layer configurations of the same thickness, a new experimental setting was performed using coatings with a total thickness of about 30 nm and thus further reducing the deposition time (from about 8 hours to about 3 hours) and the process related costs. In these experiments, only two strategies were tested, a single layer of Al₂O₃ (A, Figure 57a) and a multilayer configuration composed of 10 nm of Al₂O₃, followed by 10 alternate layers of TiO₂ and Al₂O₃ (about 1 nm for each single layer), followed by a single layer of about 10 nm of TiO₂ (B, Figure 57b). Due to the extremely low thickness of the central multilayer, intermixing between the two composition was expected.
FORTH EXPERIMENTAL SETTING

A forth experimental setting was made with coatings of a total thickness of about 10 nm. This value was considered optimal from the reduced deposition time (about 1.5 hours) and thus the low related deposition costs. The deposited coatings were a 10 nm Al$_2$O$_3$ coating (A, Figure 58a) and a 2 nm Al$_2$O$_3$ + 10 alternate layers of TiO$_2$ and Al$_2$O$_3$ of about 0.5 nm each followed by 3 nm of TiO$_2$ (B, Figure 58b).

![Figure 58: Coatings configuration for the forth experimental setting](image)

FIFTH EXPERIMENTAL SETTING

The last experimental setting was based on a completely different approach. Instead of using two different metal oxides in order to form a multilayer configuration, depositions of the same oxide at two different temperature have been made in an alternate fashion. The chosen metal oxide was Al$_2$O$_3$, due to the high corrosion resistance performances shown in literature, while the deposition temperature were 120 °C (leading to an amorphous structure of the coating) and 300 °C (leading to a crystalline structure of the coating).

Depositions were based on the following hypothesis:

- Amorphous Al$_2$O$_3$ has extremely low mechanical properties and may be easily damaged and scratched, while crystalline Al$_2$O$_3$ is hard and resistant;
- Amorphous Al$_2$O$_3$ is adherent and protective, while crystalline Al$_2$O$_3$ has poor adhesion and relatively low corrosion resistance due to the residual porosity at the grain boundaries;
- The chemical affinity between amorphous and crystalline Al$_2$O$_3$ may prevent delamination of the single layers of the coating.

To verify the previous hypothesis, three different configurations were tested: 5 nm of amorphous Al$_2$O$_3$ followed by 5 nm of crystalline Al$_2$O$_3$ (AC, Figure 59a), 5 nm of crystalline
Al$_2$O$_3$ followed by 5 nm of amorphous Al$_2$O$_3$ (CA, Figure 59b) and a triple layer formed by 5 nm of amorphous Al$_2$O$_3$, 5 nm of crystalline Al$_2$O$_3$ and then 5 nm of amorphous Al$_2$O$_3$ again (CAC, Figure 59c).

**Figure 59: Coatings configuration for the fifth experimental setting**
6 - SAMPLES CHARACTERIZATION

The coatings were tested using a wide array of techniques, in order to fully characterize their corrosion related properties. For this reason, the ALD coatings were tested by different means:

- **Atomic Force Microscopy (AFM)** both at the coating surface and at an interface region between coated and uncoated substrate;
- **Glow Discharge Optical Emission Spectroscopy (GDOES)** in order to obtain the in-depth profile of qualitative composition for all the different layers, with an accuracy of about 2 nm;
- **Scanning Electron Microscopy (SEM)** both at the coating surface and an interface region between coated and uncoated substrate;
- **Potentiodynamic Polarization Curves (PP)** in order to discriminate the electrochemical resistance to corrosion phenomena granted by the different protective layers;
- **Vickers delamination tests** were also performed in order to determine the delamination resistance of the coatings in proximity to the indentation, and a comparison between delaminated areas respect to the applied load has been made.

Due to the extremely low thickness of some coating configurations, in particular in the third, fourth and fifth experimental setting, in which the coating thicknesses were comparable if not lower than the surface roughness of the substrate, not all characterization techniques could be correctly used to obtain reliable data.
Atomic Force Microscopy

Atomic force microscopy (AFM, Figure 60) or scanning force microscopy (SFM) [1-6] is a very high-resolution type of scanning probe microscopy, with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. The precursor to the AFM, the scanning tunneling microscope, was developed by Gerd Binnig and Heinrich Rohrer in the early 1980s at IBM Research - Zurich, a development that earned them the Nobel Prize for Physics in 1986. Binnig, Quate and Gerber invented the first atomic force microscope (also abbreviated as AFM) in 1986. The first commercially available atomic force microscope was introduced in 1989. The AFM is one of the foremost tools for imaging, measuring, and manipulating matter at the nanoscale level. The information is gathered by scanning the surface with a mechanical probe. Piezoelectric elements that facilitate tiny but accurate and precise movements on (electronic) command enable the very precise scanning. In some variations, electric potentials can also be scanned using conducting cantilevers.

The AFM consists of a cantilevered probe with a sharp tip (up to ~10 atoms at the fillet radius) at its end that is used to scan the specimen surface, in a similar way compared to a record player’s pin. The cantilever is typically made of silicon or silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke’s law.

Depending on situation and necessity, forces that can be measured with AFM include mechanical contact force (Figure 61), van der Waals forces, capillary forces, chemical bonding, friction, electrostatic forces, magnetic forces (see magnetic force microscope, MFM), Casimir forces, solvation forces, etc. Along with force, additional quantities may simultaneously be measured through the use of specialized types of probe (see scanning thermal microscopy, scanning joule expansion microscopy, photothermal microspectroscopy, etc.). Typically, the
deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes. Other methods that are used include optical interferometry, capacitive sensing or piezoresistive AFM cantilevers. These cantilevers are fabricated with piezoresistive elements that act as a strain gauge. Using a Wheatstone bridge, strain in the AFM cantilever due to deflection can be measured, but this method is not as sensitive as laser deflection or interferometry.

*Figure 61: AFM scan of a polished carbon fiber reinforced PEEK sample, 20x20x0.5 microns map*

If the tip was scanned at a constant height, a risk would exist that the tip collides with the surface, causing damage. Hence, in most cases a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample, using a proportional, and integrative and a linear gain. Traditionally, the sample is mounted on a piezoelectric tube, that can move the sample in the z direction for maintaining a constant force, and the x and y directions for scanning the sample.

Alternatively a 'tripod' configuration of three piezo crystals may be employed, with each responsible for scanning in the x,y and z directions. This eliminates some of the distortion effects seen with a tube scanner. In newer designs, the tip is mounted on a vertical piezo scanner while the sample is being scanned in X and Y using another piezo block. The resulting map of the area $z = f(x,y)$ represents the topography of the sample.

The AFM can be operated in a number of modes, depending on the application. In general, possible imaging modes are divided into static (also called contact) modes and a variety of dynamic (or non-contact) modes where the cantilever is vibrated.
CONTACT MODE

In the static mode operation, the static tip deflection is used as a feedback signal. Because the measurement of a static signal is prone to noise and drift, low stiffness cantilevers are used to boost the deflection signal. However, close to the surface of the sample, attractive forces can be quite strong, causing the tip to "snap-in" to the surface. Thus static mode AFM is almost always done in contact where the overall force is repulsive. Consequently, this technique is typically called "contact mode". In contact mode, the force between the tip and the surface is kept constant during scanning by maintaining a constant deflection.

TAPPING MODE

[Image: Figure 62: DNA as seen by tapping mode AFM, 5x5x0.1 microns map]

In ambient conditions, most samples develop a liquid meniscus layer. Because of this, keeping the probe tip close enough to the sample for short-range forces to become detectable while preventing the tip from sticking to the surface presents a major problem for non-contact dynamic mode in ambient conditions. Dynamic contact mode (also called intermittent contact or tapping mode, Figure 62) was developed to bypass this problem. In tapping mode, also called "AC Mode" or "intermittent contact mode", the cantilever is driven to oscillate up and down at near its resonance frequency by a small piezoelectric element mounted in the AFM tip holder similar to non-contact mode. However, the amplitude of this oscillation is greater than 10 nm, typically 100 to 200 nm. Due to the interaction of forces acting on the cantilever when the tip comes close to the surface, Van der Waals force, dipole-dipole interaction, electrostatic forces, etc. cause the amplitude of this oscillation to decrease as the tip gets closer to the sample. An electronic servo uses the piezoelectric actuator to control the height of the cantilever above the sample. The servo adjusts the height to maintain a set cantilever oscillation amplitude as the
cantilever is scanned over the sample. A tapping AFM image is therefore produced by imaging the force of the intermittent contacts of the tip with the sample surface.

This method of "tapping" lessens the damage done to the surface and the tip compared to the amount done in contact mode. Tapping mode is gentle enough even for the visualization of supported lipid bilayers or adsorbed single polymer molecules (for instance, 0.4 nm thick chains of synthetic polyelectrolytes) under liquid medium. With proper scanning parameters, the conformation of single molecules can remain unchanged for hours.
Scanning Kelvin Probe Force Microscopy

Figure 63: Scheme of Scanning Kelvin Probe Force Microscopy

Kelvin probe force microscopy (KPFM, Figure 63) [7-10], also known as surface potential microscopy, is a noncontact variant of atomic force microscopy (AFM) that was invented in 1991.[1] With KPFM, the work function of surfaces can be observed at atomic or molecular scales. The work function relates to many surface phenomena, including catalytic activity, reconstruction of surfaces, doping and band-bending of semiconductors, charge trapping in dielectrics and corrosion. The map of the work function produced by KPFM gives information about the composition and electronic state of the local structures on the surface of a solid.

KPFM is a scanning probe method where the potential offset between a probe tip and a surface can be measured using the same principle as a macroscopic Kelvin probe. The cantilever in the AFM is a reference electrode that forms a capacitor with the surface, over which it is scanned laterally at a constant separation. The cantilever is not piezoelectrically driven at its mechanical resonance frequency $\omega_0$ as in normal AFM although an alternating current (AC) voltage is applied at this frequency.

When there is a direct-current (DC) potential difference between the tip and the surface, the AC+DC voltage offset will cause the cantilever to vibrate. The origin of the force can be understood by considering that the energy of the capacitor formed by the cantilever and the surface is plus terms at DC. Only the cross-term proportional to the $V_{DC} \cdot V_{AC}$ product is at the resonance frequency $\omega_0$. The resulting vibration of the cantilever is detected using usual scanned-probe microscopy methods (typically involving a diode laser and a four-quadrant detector). A null circuit is used to drive the DC potential of the tip to a value which minimizes the vibration. A map of this nulling DC potential versus the lateral position coordinate therefore produces an image of the work function of the surface.
A related technique, electrostatic force microscopy (EFM), directly measures the force produced on a charged tip by the electric field emanating from the surface. EFM operates much like magnetic force microscopy in that the frequency shift or amplitude change of the cantilever oscillation is used to detect the electric field. However, EFM is much more sensitive to topographic artifacts than KFPM. Both EFM and KPFM require the use of conductive cantilevers, typically metal-coated silicon or silicon nitride.

**WORKING PRINCIPLE**

The Kelvin probe force microscope or Kelvin force microscope (KFM) is based on an AFM set-up and the determination of the work function is based on the measurement of the electrostatic forces between the small AFM tip and the sample. The conducting tip and the sample are characterized by (in general) different work functions. When both elements are brought in contact, a net electric current will flow between them until the Fermi levels are aligned. The potential is called the contact potential (difference) denoted generally with VCPD. An electrostatic force between tip and sample builds up, resulting from the net charge transfer. For the measurement a voltage is applied between tip and sample, consisting of a DC-bias VDC and an AC-voltage VAC \( \sin(\omega_0 t) \) of frequency \( \omega_0 \) at the second resonance frequency of the AFM cantilever.

Tuning the AC-frequency to the second resonance frequency of the cantilever results in an improved sensitivity and allows the independent and simultaneous imaging of topography and the contact potential. As a result of these biasing conditions, an oscillating electrostatic force appears, inducing an additional oscillation of the cantilever with the characteristic frequency \( \omega_2 \). The general expression of such electrostatic force not considering coulomb forces due to charges can be written as

The electrostatic force can be split up into three contributions, as the total electrostatic force \( F \) acting on the tip has spectral components at the frequencies \( \omega_2 \) and \( 2\omega_2 \).

The DC component, \( F_{DC} \), contributes to the topographical signal, the term \( F_{\omega_2} \) at the characteristic frequency \( \omega_2 \) is used to measure the contact potential and the contribution \( F_{2\omega_2} \) can be used for capacitance microscopy.

For contact potential measurements a lock-in amplifier is used to detect the cantilever oscillation at \( \omega_2 \). During the scan VDC will be adjusted so that the electrostatic forces between the tip and the sample become zero and thus the response at the oscillation frequency \( \omega_2 \) becomes zero and at the same time response at frequency \( 2\omega_2 \) become maximum. Since the electrostatic force at \( \omega_2 \) depends on VDC - VCPD, the value of VDC which minimizes the \( \omega_2 \)-term corresponds to the contact potential. Absolute values of the sample work function can be obtained if the tip is first calibrated against a reference sample of known work function. Apart from this, one can use the normal topographic scan methods at the resonance frequency \( \omega \) independently of the above. Thus, in one scan, the topography and the contact potential of the sample are determined simultaneously.
Chapter 6: Samples Characterization
Glow Discharge Optical Emission Spectroscopy

In Glow Discharge Spectroscopy (GDOES, Figure 64) [11-17] sputtering and atomic emission are combined to provide a modern, extremely rapid technique for analysing bulk solids and depth profiling surfaces, coatings and interfaces. Provided it is compatible con vacuum, GD-OES can analyse practically any solid material. GD-OES is now being used routinely to analyse industrial and research materials: to determine, for example, the composition of metallic alloys, polymers, layered semiconductor and glasses, the distribution of elements in metallic and polymer coatings, the levels of hydrocarbons and the composition of passivation and corrosion layers on surfaces.

In a glow discharge source, two parallel plates, one the cathode and the other the anode, are separated by some centimeters in a glass vacuum tube, and a carrier gas (Argon) is introduced and a potential difference applied across the plates. When the gas pressure and potential difference are at suitable values, depending on the composition of the gas and the cathode, the source is seen to glow strongly, in bright and dark bands between the cathode and the anode. When the current is sufficiently high, the cathode is fully covered by dark space. Some millimetres from the cathode is the bright band, called the negative glow, this is then followed by a dark band and then another bright band, called the positive column, which extends almost to the anode. When the anode is brought closer to the cathode, the positive column disappears and the dominant features remaining are the cathode dark space and the negative glow. This abnormal state is the working condition of GD-OES.

In the cathode dark space, the argon is ionised and the argon ions produced there bombard the cathode surface causing sputtering of the cathode. Sputtered materials from the cathode passes
back through the cathode dark space and enters the negative glow region where it is excited and
glows brightly by atomic emission. The emission lines are then detected to analyse the material
being sputtered from the cathode. If the potential applied across the cathode and the anode is
constant (dc) then the conductive materials can be analysed, if the potential is varying at radio
frequency (rf) then both conductive and non-conductive materials can be analysed.

The most important source used to date in GD analysis is the Grimm source. The more recent
Marcus source has many features in common with the Grimm source. In the Grimm source, the
anode is no longer a flat plate but a hollow copper tube, the annular face of the tube stopping
only 0.1-0.2 mm from the surface of the sample which acts as the cathode. The spacing between
the anode and sample, d, is smaller than the dark space so that no discharge is possible there,
both of the sputtering of the sample surface occurs in the region opposite the hollow of the
anode. When the current-potential-pressure conditions are optimised inside the source then
very flat and very fast sputtering of the sample occurs.

The optical layout of a simple GD-OES instrument is composed by few components. The emitted
light or, more correctly, the emitted photons (since the recorded wavelengths extend well below
the visible region of 400-700 nm, down to 110 nm in the far vacuum ultraviolet) pass through
the source windows and the into an optical spectrometer. The spectrometer can be either a
dichromator, i.e. a spectrometer with many fixed channels each set to a different wavelength
for recording many elemental signals simultaneously, or a monochromator, i.e. a spectrometer
with one channel where the spectrometer is tunable over a wide wavelength range.

During operation, the applied potential (or self-bias in the rf case), causes electrons to flow with
high energy from the sample surface towards the anode. The electrons and argon interact to
form a plasma. In this plasma, most of the potential is dropped across the cathode dark space in
front of the sample. The high-energy electrons there collide with argon atoms causing a positive
ionisation of the argon. The positive argon ions then are driven by the negative bias in the
cathode dark space to collide with the sample surface. Along the way the argon ions suffer other
collisions and lose, on average, about half of their energy. There is still sufficient kinetic energy
to cause sputtering of the sample surface. The sputtered atoms move away from the surface
where they suffer many collisions with the argon and very rapidly slow to thermal speeds of
around 500 m/s. At the edge of the cathode dark space and into the negative glow region there
are plenty of electrons with sufficient energy (greater than about 4 eV) to cause excitation.
Argon atoms are also excited in this region into their metastable state and collisions with
metastable argon atoms can also cause excitation of the sputtered atoms. Once excited, the
sputtered atoms then deexcite by emitting photons with characteristics wavelengths (called
emission lines). For example, the familiar yellow doubled from sodium, at 589.00 and 589.59
nm.

The impact of the argon ions and the subsequent sputtering of the sample surface is a fairly
random process –at least on atomic scale – and some areas will be eroded by chance more
quickly than others. Sputtering is not purely random, through. When dealing with real surfaces,
i.e. the surface of complex multi-component solids, different components will sputter at
different rates. Some elements will sputter preferentially, causing a change in surface
concentration. Eventually a steady state is reached, through the conservation of the mass, where elements are sputtered at a rate proportional to the underlying stoichiometry. The depth for steady state sputtering is comparable with the depth of penetration of the incident ions.

Differential sputtering effects can lead to changes of roughness, i.e. the corrugations of the crater bottom, with depth. During sputtering at depths between 5 and 20 um, the roughness of the crater bottom can change markedly, suggesting a change from random to local-orientation weighted sputtering at about this depth. The biggest effect on depth resolution, however, is often not the statistical nature of sputtering but the overall shape of the crater bottom, so the crater bottom should be as flat as possible.
SCANNING ELECTRON MICROSCOPE

The scanning electron microscope (SEM, Figure 65) [18-19] uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 300,000X, spatial resolution of 5 to 10 nm).

The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using Electron Diffraction Spectroscopy, EDS), crystalline structure, and crystal orientations (using Electron Backscattered Diffraction, EBSD). The design and function of the SEM is very similar to the Electron Probe Micro Analyzer (EPMA) and considerable overlap in capabilities exists between the two instruments.

Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light
(cathodoluminescence--CL), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive"; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyse the same materials repeatedly.
All corrosion is an electrochemical process of oxidation and reduction reactions. As corrosion occurs, electrons are released by the metal (oxidation) and gained by elements (reduction) in the corroding solution. Because there is a flow of electrons (current) in the corrosion reaction, it can be measured and controlled electronically. Therefore, controlled electrochemical experimental methods can be used to characterize the corrosion properties of metals and metal components in combination with various electrolyte solutions. The corrosion characteristics are unique to each metal/solution system.

In testing practice, a polarization cell (Figure 66) is setup consisting of an electrolyte solution, a reference electrode, a counter electrode(s), and the metal sample of interest connected to a specimen holder. (The sample is called the working electrode.) The electrodes are connected to an electronic instrument called a potentiostat. The working, reference, and counting electrodes are placed in the electrolyte solution, generally a solution that most closely resembles the actual application environment of the material being tested. In the solution, an electrochemical potential (voltage) is generated between the various electrodes. The corrosion potential ($E_{CORR}$) is measured by the potentiostat as an energy difference between the working electrode and the reference electrode.

Electrochemical corrosion experiments measure and/or control the potential and current of the oxidation/reduction reactions. Several types of experiments are possible by manipulating and measuring these two variables.

Most experiments impose a potential on the working electrode and measure the resulting current. A potentiostatic experiment imposes a constant potential on the working electrode for a specific time period. The measured current is plotted verses time.

For potentiodynamic experiments, the applied potential is increased with time while the current is constantly monitored. The current (or current density) is plotted verses the potential. After
the potential is scanned to a predetermined current density or potential, the potential scan may be reversed while the current continues to be measured. A potentiodynamic scan like this is referred to as reverse polarization or cyclic polarization.

It is also possible to control the current and measure the resulting potential. Experiments where the current is imposed rather than the potential are referred to as galvanodynamic or galvanostatic.

Galvanodynamic methods plot the variation in potential verses the controlled current. Galvanostatic tests maintain a constant current and plot the change in potential verses time.

Potentiodynamic experiments can provide a variety of data related to the pitting, crevice corrosion, and passivation behavior for specific sample/solution combinations. As the potential is increased, pitting corrosion will begin at a certain value known as the breakdown potential (EB, the lowest potential at which pitting occurs). Since pitting corrosion relates to an increase in the oxidation rate, the EB is determined by the corresponding increase in measured current. An increase in EB is associated with higher resistance to pitting corrosion. As the potential is decreased on the reverse scan, there is a decrease in the current. However, hysteresis is observed for the reverse scan and a hysteresis loop is traced. The sample is repassivated at the potential where the reverse scan crosses the forward scan. The repassivation potential, or protection potential (EP), occurs at a lower potential than the EB. The difference between EB and EP is related to susceptibility to crevice corrosion; the greater the hysteresis in the polarization curve, the greater the crevice corrosion susceptibility.

Electrochemical corrosion experiments may also be used to determine corrosion rates (Tafel Plot), active/passive characteristics for a specific sample/solution system, passivation rates, and anodic and cathodic protection.
As ALD coatings proved to be ineffective for the protection of the substrate against wear, due to the low tribological resistance of vitreous ceramic layers, conventional delamination testing methods couldn’t be applied to the samples. In addition, the ALD thickness resulted to be too limited to be resolved using optical observations or conventional microscopes. For this reason, a different test has been applied, based on conventional Vickers indentations at different loading conditions.

In Vickers delamination test, a conventional Vickers microhardness tester is used in order to apply a known load on a coated sample. After the removal of the load, the sample surface is cleaned using an ethanol ultrasonic bath and then observed at SEM.

Repeating this procedure at increasing loads, it is possible to plot a graph of the delaminated area surrounding the indentation against the indentation load. These graphs cannot be used to obtain an absolute measurement of the delamination resistance of the applied coatings, as they are influenced by the applied load, but proved to be effective for a comparison of the delamination resistance between different coatings with the same thickness and/or with coatings with different thicknesses.
REFERENCES


Chapter 6: Samples Characterization
7 - RESULTS

FIRST EXPERIMENTAL SETTING

Figure 68: AFM maps as obtained on the AISI 316L 2D (a) and 2B (b) finishings

Figure 68 shows the morphology of the AISI 316L substrates with a standard 2D (a) and 2B (b) finishing. In Figure 68a the grain boundaries of AISI 316L stainless steel were etched by the aggressive acid bath, resulting in deep and narrow porosities which completely altered the morphology of the sample's surface and clearly enlightening the microstructure of the steel with an average grain diameter of about 30 μm. In Figure 68b, the lamination direction can be easily deduced by the presence of oriented lines from the upper to the lower part of the image. Grain boundaries are in this case softly enhanced by the skinpassing process and a martensitic structure can be identified on the surface of some grains, proving that ε-martensite was formed due to the cold deformation. Nevertheless, the mean grain diameter is quite similar if compared to Sample A. The substrate roughness in the two cases resulted to be strongly different: the 2D finishing showed a surface roughness of about 400 nm, while the 2B finishing showed a surface roughness of about 50 nm. Both morphologies resulted to be completely unaltered by the application of the 280 nm ALD bilayer coating.

Figure 69: SEM images obtained on the AISI 316L 2D (a) and 2B (b) finishings
Images obtained on both finishing at SEM (Figure 69) clearly showed similar results when compared to AFM maps on the similar regions of the sample. In Figure 69a the etched grain structure of the standard 2D finishing is presented, while the oriented morphology of the skinpassing process is clearly visible on Figure 69b. No coating defects, lacks of adhesion, blistering phenomena or local anomalies were observed at the SEM on the whole surface of the samples.

**Figure 70: GDOES profile as obtained on the 280 nm coated sample**

The GDOES profiles of sample B was selected to be shown in Fig. 70 due to the lower surface roughness which allows better evaluating the coating-substrate interface. Profiles obtained on sample A are quite similar, but much more affected distributed signals and not sharp interfaces. The presence of the two ALD layers is well evident. The increase in the chromium and iron signals reveals the presence of the steel substrate. Then the whole coating thickness is in the range of 280 nm where the signals of aluminium and oxygen fall.

Due to the roughness of the substrate (about 60 nm) the Al₂O₃ layer thickness cannot be precisely identified in the graph. Presence of aluminium can be found from about 180 up to 350 nm. The titanium layer is thicker and its signal starts to decrease at about 170 nm but it is clearly visible up to 350 nm. Interdiffusion and inter-mixing phenomena between the two ALD layers’ signals are probably due to the roughness of the substrate and the different sputtering rate of the two layers and not caused by a real diffusion phenomena occurred during deposition, as the deposition temperature of about 120 °C was considered insufficient to cause diffusion of ions between ceramic layers, which have also often been used as ion diffusion barrier in literature.
The higher peak near the free surface is both caused surface water absorption and the hydrogen effect deeply discussed by Payling et al. [1].

GDOES analysis also showed that the picking treatment caused no sensible variation of the surface carbon content between the two samples.

**Figure 71: Polarization curves for sample B**

Polarization curves in Figure 71 show that AISI 316 stainless steel is naturally corrosion resistant, with a passive region of about 0.6 V and passive current densities in the range of $10^{-7}$ A/cm$^2$. Sample B shows higher passive current density with respect to sample A. This could be easily associated to the presence of superficial ε-martensite which is well known for its lower corrosion resistance when compared to austenite. For Sample A, passivity breakdown occurs around 0.8 V respect to Ag/AgCl, while Sample B passivity breakdown clearly occurs at lower values, around 0.65 V respect to Ag/AgCl, which might be the effect of the higher surface roughness, where pitting corrosion phenomena are more prone to trigger at the crevices present at the grain boundaries.

Deposition of nanometric ALD coatings greatly improves the corrosion resistance of both pickled or skinpassed stainless steel substrates eliminating any possible roughness effect. This result is clearly visible in Fig. 25. Both substrates showed totally comparable passive current densities which decrease from $10^{-7}$ to less than $10^{-9}$ A/cm$^2$ and passive potential ranges (up to 1.2 V), where breakdown potentials are shifted towards more positive values, almost in the transpassive region.
Figure 72 shows an AFM map as obtained on Sample B at about 5 diagonals from a Vickers indentation (HV_{0.3}) and was used in order to evaluate the adhesion of the 280 nm thick ALD coating to the substrate. A large delaminated area surrounded by a wide net of cracks was enlightened around the Vickers indentation due to the fragile and vitreous nature of the amorphous ALD coating. Since relatively far from the indentation the coating was cracked but no delaminated, the presence of coating defects in this region could not be resolved by SEM observations, due to the transparency of the nanometric ALD layer to the Electron Beam and was only observed by AFM.

As the presence of an indentation clearly showed consequences on the integrity of the coating at about 5 indentation diagonals, the mechanical characteristics of the 280 nm coating were considered to be too low for any possible real industrial application, even if the corrosion protection offered to the substrate by this strategy was extremely promising.

The coating deposition time, about 10 hours comprised of loading procedure, vacuum pumping and unloading procedure, was considered to be too long and thus too expensive to really be competitive at an industrial level.
SECOND EXPERIMENTAL SETTING

AFM maps obtained on the coated surface of the different samples, 100 nm TiO$_2$ (A), 100 nm Al$_2$O$_3$ (B), 50 nm Al$_2$O$_3$/50 nm TiO$_2$ (C) and Al$_2$O$_3$/TiO$_2$/Al$_2$O$_3$/TiO$_2$ 25 nm each (D)

AFM proved to be strongly influenced by the planarity of the investigated surface. Since the samples were polished and the surface roughness features very smooth, vertical image resolution was big enough to be compared with surface curvature and roughness. To compensate this phenomenon, post-processing software was used in order to flatten the acquired AFM map.

Fig. 73 shows the bi-dimensional AFM 50x50 micron maps of the four samples after ALD deposition. For all samples the morphology is flat and the roughness quite low (about 20 nm Ra). In all cases, smooth, oriented linear scratches due to the polishing procedure are evident along the maps. Few spot-like spikes caused by small dust particles are present on the maps for coatings B, C and D, while the surface of coating A appeared completely covered by 1 micron diameter 20 nm high peaks that may be caused by small local adhesion defects between ALD TiO$_2$ and Steel substrate. No cracks or delamination phenomena were found on the samples during AFM analysis.
Fig. 74 shows the interface region of the four samples in tri-dimensional AFM 10x10 micron maps. In all cases it is evident that the pristine micro-roughness of the substrate is maintained and mirrored in the ALD coating surface. Some interface defects between coated and uncoated regions are caused by the removal of the laboratory adhesive tape or its incomplete adhesion to the substrate. In the cross-section linear scans the approximate coating thickness is calculated by specific AFM image analysis software (Fig. 75). Mean thickness values were then obtained using ten linear measures for each different sample (Tab. 14).

**Table 17: AFM thickness values as measured at the interface between coated and uncoated regions of the samples**

<table>
<thead>
<tr>
<th></th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Al₂O₃/TiO₂</th>
<th>2x(Al₂O₃/TiO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nm</td>
<td>nm</td>
<td>nm</td>
<td>nm</td>
<td>nm</td>
</tr>
<tr>
<td>92 ± 8</td>
<td>130 ± 11</td>
<td>102 ± 7</td>
<td>107 ± 8</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 76 shows the SKPFM maps obtained on the same interface regions of the morphological maps of Fig. 74. The color convention chosen for these maps was yellow for higher Volta Potential and red for lower Volta Potential. The interface between coating and substrate is smoother than that obtained in morphological maps. This is due to the fact that the Volta Potential measured in one point is an average of the contribution of all points surrounding the probe, so at the interface region both coating and substrate potentials are still detected resulting in an average value on the map and not in a sharp interface, as electrical signal are omnidirectional.
Fig. 76a shows a different behavior respect to the other images. Table 15 shows the results of SKP-FM tests performed using AFM. All samples coated with at least one layer of Al₂O₃ (B, C and D) showed a lower Volta potential compared to the AISI 316 L substrate, while the coating of TiO₂ present on Sample A resulted to have a higher Volta potential respect to the AISI 316 L substrate, which may be related to the nature of the TiO₂ coating, which is considered a semiconductor and as a consequence, has a cathodic behavior compared to the conductive metallic substrate of AISI 316 Stainless Steel. Coating B, completely made of Al₂O₃, showed the lowest Volta potential between the four coatings, meaning that ALD Al₂O₃ deposited at 120 °C shows the natural behavior of standard non-conductive ceramic materials, which appear to be more anodic due to their pure resistive electrical behavior. Coating C and Coating D, as predictable, show a less negative Volta Potential respect to Coating B thanks to the presence of both TiO₂ and Al₂O₃.

**TABLE 18: SKP-FM DIFFERENCES IN VOLTA POTENTIAL AS MEASURED AT THE INTERFACE BETWEEN COATED AND UNCOATED REGIONS OF THE SAMPLES**

<table>
<thead>
<tr>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Al₂O₃/TiO₂</th>
<th>2x(Al₂O₃/TiO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>V</td>
<td>V</td>
<td>V</td>
</tr>
<tr>
<td>+120 ± 11</td>
<td>-210 ± 14</td>
<td>-140 ± 16</td>
<td>-97 ± 19</td>
</tr>
</tbody>
</table>

The results obtained by this technique suggest that Al₂O₃ obtained by ALD at 120 °C has a completely different electrochemical behavior when compared to TiO₂ obtained by ALD at the same temperature. Multilayer configurations show intermediate behaviors due to the presence of both layers at the same time. From an electrochemical point of view, both solutions may be efficient for the corrosion protection of the substrate, in the case of defect-free coatings. When defects are present, the TiO₂ coatings may result in galvanic coupling between the coating and the substrate in proximity of the defect, which may promote and/or enhance the corrosion rate of the sample in aggressive media.

**Figure 77:** SKP-FM linear scan at the interface between coated and uncoated regions as obtained for the TiO₂ coated sample (A).
Figures 78 to 81 show the in-depth compositional profile of the four samples as obtained using calibrated GDOES analysis. All the four samples were investigated for the first 200 nm of thickness in order to correctly resolve and calculate the interface point between coating and substrate. GDOES accuracy was strongly related to the sharpness of the interface region between coating and substrate, which can be considered mainly a function of the surface roughness but is also influenced by the different sputtering rates between metallic substrate and ceramic coatings and the resolution limits of the GDOES instrument, which is considered to be around 2 nm.

As different conventions may be applied to GDOES measurements to calculate the thickness of a coating, in this work the coating thickness is measured between the free surface and the point in which the coating signals (in weight percent) are surpassed by the substrate signals. This convention was chosen mainly because of the applicability of the method to all ALD coated samples, which leads to fast and reliable measurements.

![GDOES Results Graph](image)

**Figure 78: GDOES Results for the First 200 nm of the 100 nm TiO₂ Sample (A)**

Fig. 78 shows the GDOES graph for the first 200 nm of sample A. The thickness of the coating resulted to be around 95 nm, even if, due to the roughness of the surface, coating signals are still present till 140 nm. The coating composition resulted to be around 75% oxygen and 25% titanium in weight, which is far from the 60% titanium 40% oxygen of TiO₂. This strong oxygen overestimation is considered to be caused by the absence of conformal standards for amorphous ceramic materials in the GDOES calibration method. Since the measured thickness is close to the values obtained by AFM, the GDOES can be considered reliable for thickness determination but only qualitative in the compositional evaluation. The initial, small oxygen peak (about 10 nm) can be caused both by water adsorbed at the coating’s surface and the
hydrogen effect, which causes an overestimation of the gaseous elements during GDOES analyses.

![GDOES Results](image)

**Figure 79: GDOES Results for the First 200 nm of the 100 nm Al₂O₃ Sample (B)**

Fig. 79 shows the GDOES graph for the first 200 nm of Sample B. The thickness of the coating resulted to be around 105 nm, even if coating signals are present till 150 nm. As before, this is due to the surface roughness of the sample and the difference in sputtering rates between ceramic coating and steel substrate. The coating composition resulted to be around 90% oxygen and 10% aluminum in weight, which is far from the 53% aluminum 47% oxygen in weight of standard Al₂O₃. In this case the oxygen signal overestimation is really stronger than expected. This can still be caused by the absence of reliable standards for GDOES calibration, even if the amorphous structure of the Al₂O₃ layer may also play a role in the calibration process of the instrument, considering that crystalline and amorphous structures may have intrinsic differences in the sputtering rates. Since the measured thickness is close to the values obtained by AFM, even in this case the GDOES can be considered reliable for thickness analysis but qualitative in the compositional analysis.
Fig. 80 shows the GDOES graph for the first 200 nm of Sample C. The thickness of the coating resulted to be around 102 nm, even if oxygen signals are present till 130 nm and aluminum signals till 160 nm. This is due to the surface roughness of the sample and the difference in sputtering rates between ceramic coating and steel substrate. The interface between the two different layers can be estimated to be around 60 nm, even if a strong inter-diffusion of the Titanium and Aluminum signals is present, in the region between 40 and 120 nm. The coating composition resulted to be around 80% oxygen and 15% aluminum in weight for the Al₂O₃ layer and about 30% Titanium and 70% Oxygen for the TiO₂ layer. Both compositions are far from their stoichiometry. In this case the oxygen signal overestimation is far stronger than expected. This can still be caused by the absence of reliable standards for GDOES calibration. Since the measured thickness is close to the values obtained by AFM, even in this case the GDOES can be considered reliable for thickness analysis but qualitative in the compositional analysis.
Fig. 81 shows the GDOES graph for the first 200 nm of Sample D. The thickness of the coating resulted to be around 96 nm, even if oxygen signals are present till 180 nm and aluminum signals till 160 nm. This is due to the surface roughness of the sample and the difference in sputtering rates between ceramic coating and steel substrate. The interfaces between the four different layers can be estimated to be around 30, 55 and 80 nm, even if a strong inter-diffusion of the Titanium and Aluminum signals is present, for the whole coating thickness and in particular from 60 to 160 nm. Since the measured thickness is close to the values obtained by AFM, even in this case the GDOES can be considered reliable for thickness analysis but qualitative in the compositional analysis.

The thickness values obtained for each layer and for each different sample are resumed in Table 16:

### Table 19: Layer thickness for each different layer of the four samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>1st layer</th>
<th>2nd layer</th>
<th>3rd layer</th>
<th>4th layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 nm TiO₂</td>
<td>95</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100 nm Al₂O₃</td>
<td>105</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>50 nm Al₂O₃ / 50 nm TiO₂</td>
<td>60</td>
<td>42</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25 nm Al₂O₃ / 25 nm TiO₂ / 25 nm Al₂O₃ / 25 nm TiO₂</td>
<td>31</td>
<td>23</td>
<td>27</td>
<td>15</td>
</tr>
</tbody>
</table>
The resistance of the coating to delamination has been evaluated using standard Vickers microhardness indentations at different loads and measuring the delaminated areas surrounding the indentation. This method has proved to be strongly affected by statistical errors and showed a great dispersion in the results, which is quite explainable taking into account the amorphous-glasslike behavior of the nanometric ALD films. Twenty measurements were performed for each load value, in order to obtain reliable statistical data.

![Delaminated Area](image)

**Figure 82**: Vickers delamination results as Area/Load plotted against normal load, with applied loads of 1, 2, 5, 10, 20 N

The Vickers indentation performed at 1, 2, 5, 10 and 20 N of normal load has been plotted against the normalized delamination area over load ratio. This ratio was chosen in order not to have un-comparable values differences between low and high loads. The obtained results are shown in Figure 82. It can be observed that the ratio is almost constant for each sample at normal loads of 10 N or higher, which implies a linear dependency of the Area on the applied Load. On the contrary, at normal loads lower than 10 N, each coating clearly showed a different behavior. For the overall investigated load interval, sample A showed the worst behavior, with delaminated areas more than three times higher than the other samples at the lowest load (700 μm² against the 200 μm² of sample C) and close to two times higher at the highest load (1400 μm² against the 800 μm² of sample C). This behavior could be due to the lower mechanical properties of the TiO₂ and could also be related to the presence of residual chlorine in the layer, resulting in the particular morphology observed by AFM analysis suggesting the presence of micro-blisters underneath the ALD coating that may influence negatively the adhesion of the nanometric layer. The presence of these blisters is at the moment not well understood, but may also be caused by gas trapping during deposition or to a not perfect cleaning of the surface.
Literature results already shown in the past years that a TiO$_2$ layer obtained by TiCl$_4$ precursors is prone to be defective. Sample C showed higher delamination in the medium load region compared to the pure Al$_2$O$_3$ and the four layer configuration. This may be explained considering the relatively high thickness of the TiO$_2$ layer that, due to its lower mechanical properties, may have favored the coating failure. Sample B and Sample D showed a similar behavior at higher loads, while they clearly differ at the lowest load. Indeed, Sample D showed a lower delamination, close to zero up to 4.9 N. This result may be the effect of the multilayer structure that, thanks to the lower thickness per layer, reduces the overall residual stresses in the coating.

![Polarization curves as obtained from the different ALD configurations](image)

**Figure 83: Polarization curves as obtained from the different ALD configurations**

Polarization curves for the different samples are shown in Fig. 83. Uncoated AISI 316 L clearly shows a passive behavior in the 9 g/l NaCl solution, with a corrosion current density between $10^{-6}$ and $10^{-7}$ A/cm$^2$ and a passive region from 0.1 to 0.4 V with respect to Ag/AgCl. The Open Circuit Potential (OCP) for uncoated AISI 316 L steel resulted to be about 0.1 V with respect to Ag/AgCl. All four ALD coated samples showed a shift of the OCP to about -0.3 V respect to Ag/AgCl. Sample A showed a reduction of the Corrosion Current Density to less than $10^{-7}$ A/cm$^2$ and a passive region from -0.3 to 0.2 V respect to Ag/AgCl. Sample B, C and D showed a stronger corrosion current density reduction, to less than $10^{-10}$ A/cm$^2$ with wider passive regions and a shift of the breakdown potential quite over 0.6V respect to Ag/AgCl. The protective properties against localized corrosion of the stainless steel are clearly proved by the polarization curves and seems to be almost independent on the chemical or structural (mono or multilayers) characteristics of the ALD coatings. The slightly worse behavior of the TiO$_2$ coated sample could still be related to the presence of the micro-blisters and residual chlorides which could affect the barrier properties of the ceramic layer.
The polarization curves obtained from Sample A seem to be less performing than the ones obtained by Shan et al. [15] on a thinner ALD layer which was obtained by titanium isopropoxide. Our worse results could probably be due to the presence of residual chlorides. Similar comparisons can be made between Sample B and the Plasma Enhanced ALD (PE-ALD) 100 nm thick Al₂O₃ coatings obtained by Potts et al. [22], demonstrating the efficiency of the Plasma Enhanced technology. Nevertheless, multilayer ALD configurations based on two and four alternate layers of TiO₂ and Al₂O₃ proved to grant an even higher corrosion resistance without external energy source requirements.
Fig. 84 shows the GDOES graph for the first 80 nm of the sample coated with about 30 nm of Al₂O₃ (Sample A). The thickness of the coating resulted to be close to 33 nm, even if coating signals are still present at about 45 nm due to the surface roughness and the differences in sputtering rates between coating and substrate.

Reducing the coating thickness, the maximum resolution of the GDOES instrument becomes more and more important in order to correctly resolve the interface between coating and substrate and thus measure the coating thickness.

The composition of Sample A, as measured by the GDOES, resulted affected by the same calibration problems already observed for the similar 100 nm thick coating.
Fig. 85 shows the GDOES graph for the first 60 nm of the sample coated with about 30 nm of multilayered Al₂O₃/TiO₂ (Sample B). The thickness of the coating resulted to be close to 28 nm, even if signals from the coatings are still present at more than 40 nm, and the Al signal strong up to more than 30 nm.

The thickness values obtained by GDOES are resumed in Table 17. In this case the resolution of the GDOES instrument (about 2 nm) is not sufficient in order to discriminate the singular layers that compose the coating, which appears composed by a singular layer with a gradient composition, Ti-rich near the open surface and Al-rich near the coating/substrate interface. This is caused by the presence of two thicker layers (about 8 nm) composed by the two different oxide in these regions, respectively.

**Table 20: Thickness values obtained by GDOES on the different samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 nm Al₂O₃ (A)</td>
<td>33</td>
</tr>
<tr>
<td>Multilayer (B)</td>
<td>28</td>
</tr>
</tbody>
</table>
The graph of Figure 86 clearly shows the effect of the multilayer structure on the delamination resistance of the 30 nm ALD layers, presented in a logarithmic scale. Both curves resulted to be lower when compared to the curves relative to the 100 nm thick coated samples, meaning that the resistance to delamination is higher on ALD samples coated with thinner layers. This fact is well known in the field of surface technology, as higher coating thicknesses result in lower mechanical resistance to stress and deformation and higher internal tensions that may lead to cracks and defects. In particular, it can be observed that the delamination graph of Figure 40 can be divided in two different regions: at low loads (1 and 2 N), the delamination measured is about one order of magnitude lower when compared to the delamination measured at high loads (10 and 20 N).

For the whole load interval of the test, 1 N to about 20 N, the curve relative to the monolayer (Sample A) is higher when compared to the curve of the multilayer structure (Sample B), in a similar way as observed before for the four layer configuration of the 100 nm thick coatings. This is mainly caused by the beneficial effect of multilayer configurations in reducing the internal tensions of the deposited layers.
Polarization curves for the different samples are shown in Fig. 87. Uncoated AISI 316 L clearly shows a passive behavior in the 9 g/l NaCl solution, with a corrosion current density between $10^{-6}$ and $10^{-7}$ A/cm$^2$ and a passive region from 0.1 to 0.4 V with respect to Ag/AgCl. The Open Circuit Potential (OCP) for uncoated AISI 316 L steel resulted to be about 0.1 V with respect to Ag/AgCl.

Both ALD coated samples showed a shift of the OCP to about -0.25 V respect to Ag/AgCl. Sample A showed a reduction of the Corrosion Current Density to less than $10^{-7}$ A/cm$^2$ and a passive region from -0.2 to 0.6 V respect to Ag/AgCl, while Sample B showed a stronger corrosion current density reduction, to less than $10^{-9}$ A/cm$^2$ with a similar passive region of about 0.7 V and a shift of the breakdown potential to about 0.5 respect to Ag/AgCl.

The protective properties against localized corrosion of the stainless steel are clearly proved by the polarization curves and seem to be dependent on the characteristics and structure of the ALD coatings, as the multilayer configuration proved to be more effective against corrosion, in particular reducing the corrosion current density of about two orders of magnitude.

The slightly worse behavior of Sample A could be related to a higher presence residual porosity of the ALD coating which lead to a contact between aggressive media and samples substrate. In the case of the multilayer structure, each layer may have an effect in reducing the residual porosity of the previous ones, reducing the exposed substrate area and thus reducing the corrosion current density.
Corrosion resistance results obtained by the 30 nm ALD coatings proved to be limited when compared to the ones obtained using 100 nm configurations, which showed stronger corrosion current density reductions and wider passive ranges.
FORTH EXPERIMENTAL SETTING

Even if AFM resolution was small enough to correctly resolve the 10 nm ALD layers, no maps with a clear interface were obtained from the samples, probably due to the surface roughness of the substrate, higher respect to the overall coating thickness.

Due to the extremely low thickness of the 10 nm ALD coatings, GDOES compositional analyses could not be obtained. The surface roughness of the substrate, about 20 nm Ra, was in fact higher than the coating thickness itself, giving a strong overlap of signals, enhanced by the differences in sputtering rate between ceramic coating and substrate.

The GDOES resolution, about 2 nm, was also considered to be too close to the coating thickness in order to give reliable results. In the multilayer configuration (Sample B), in particular, due to the really low single layer thickness of about 0.5 nm, the GDOES was considered to be not suitable for the characterization.

![Polarization Curves](image)

**Figure 88: Polarization curves as obtained from the different ALD configurations**

Polarization curves for the different samples are shown in Fig. 88. Uncoated AISI 316 L clearly shows a passive behavior in the 9 g/l NaCl solution, with a corrosion current density between $10^{-6}$ and $10^{-7}$ A/cm² and a passive region from 0.1 to 0.4 V with respect to Ag/AgCl. The Open Circuit Potential (OCP) for uncoated AISI 316 L steel resulted to be about 0.1 V with respect to Ag/AgCl.

Both ALD coated samples showed a slight shift of the OCP to about 0 V respect to Ag/AgCl. Sample A showed a reduction of the Corrosion Current Density to less than $10^{-7}$ A/cm² and a passive region from -0.2 to 0.6 V respect to Ag/AgCl. Sample B showed a stronger corrosion current density reduction, to less than $10^{-9}$ A/cm² with a similar passive region of about 0.7 V and a shift of the breakdown potential to about 0.5 respect to Ag/AgCl.
The protective properties against localized corrosion of the stainless steel are clearly proved by the polarization curves and seem to be dependent on the characteristics and structure of the ALD coatings, as the multilayer configuration proved to be more effective against corrosion, in particular reducing the corrosion current density of about two orders of magnitude.

The slightly worse behavior of the \( \text{Al}_2\text{O}_3 \) coated sample (Sample A) could be related to a higher presence residual porosity of the ALD coating which lead to a contact between aggressive media and samples substrate. In the case of the multilayer structure, each layer may have an effect in reducing the residual porosity of the previous ones, reducing the exposed substrate area and thus reducing the corrosion current density.
FIFTH EXPERIMENTAL SETTING

**Figure 89: GDOES results for the first 30 nm of the Amorphous/Crystalline sample (AC)**

Fig. 89 shows the GDOES graph for the first 30 nm of the 10 nm Amorphous/Crystalline Al₂O₃ sample (AC). The thickness of the coating resulted to be around 17 nm, even if, due to the roughness of the surface, coating signals are still present till 40 nm. The measured thickness is higher than expected from the deposition rates of Al₂O₃. This is caused by the different temperature of deposition of the crystalline layer, which probably influenced the deposition rates of the precursors. The coating composition resulted to be around 75% oxygen and 25% aluminum in weight for the amorphous layer, which resulted to be about 7 nm thick and around 70% oxygen and 30% aluminum for the crystalline layer, which resulted to be about 10 nm thick. The strong oxygen overestimation for both layers is considered to be caused by the absence of conformal standards for both amorphous and ceramic materials in the GDOES calibration method.
Fig. 90 shows the GDOES graph for the first 50 nm of the 10 nm Crystalline/Amorphous Al$_2$O$_3$ sample (CA). The thickness of the coating resulted to be around 30 nm, even if, due to the roughness of the surface, coating signals are still present till 60 nm. The measured thickness is higher than expected from the deposition rates of Al$_2$O$_3$. This is caused by the different temperature of deposition of the crystalline layer, which probably influenced the deposition rates of the precursors.

A strong iron diffusion in the ALD coating can be observed for about 10 nm. This is probably formed during the deposition of the crystalline layer at 300 °C, which may be sufficient for a ionic diffusion from the substrate to the coating. The coating graph can be divided in two different regions: at the interface and for about 25 nm the coating composition seem to be 60% oxygen, 20% aluminum and 20% diffused iron, while the second, external layer seems composed by 90% oxygen and 10% aluminum. The strong oxygen overestimation for both layers is considered to be caused by the absence of conformal standards for both amorphous and ceramic materials in the GDOES calibration method.
Fig. 91 shows the GDOES graph for the first 80 nm of the 20 nm Crystalline / Amorphous / Crystalline Al₂O₃ sample (CAC). The thickness of the coating resulted to be around 40 nm, even if, due to the roughness of the surface, coating signals are still present till about 80 nm. The measured thickness is doubled respect to what was expected taking into account the deposition rates of Al₂O₃. This is caused by the different temperature of deposition of the crystalline layer, which probably influenced the deposition rates of the precursors.

The interface between coating and substrate is broad, probably due to the iron inter-diffusion also observed for the previous sample, even if the iron signal seems to be smoother and an almost constant iron signal region is not present for this coating. In this case, the coating signal cannot be divided in different regions, probably due to the presence of two crystalline layers deposited at 300 °C which may have an influence on the central, thinner, amorphous layer. In particular, during the deposition of the second crystalline layer, the amorphous layer is heat treated, becoming more similar to the crystalline one. For this sample, even the slight different composition revealed in the amorphous/crystalline coating was not observed. The thickness values obtained by GDOES are resumed in Table 18.

**Table 21: Thickness values as obtained by GDOES on the different samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>thickness (Nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline/Amorphous (CA)</td>
<td>17</td>
</tr>
<tr>
<td>Amorphous/Crystalline (AC)</td>
<td>30</td>
</tr>
<tr>
<td>Crystalline/Amorphous/Crystalline (CAC)</td>
<td>40</td>
</tr>
</tbody>
</table>
The graph of Figure 92 clearly shows the differences in delamination resistance between the three different samples, Amorphous/Crystalline, Crystalline/Amorphous and Crystalline/Amorphous/Crystalline. It can be observed that, for the configurations based on two layers, the resistance to delamination is higher when the first applied layer is amorphous. The three layers configuration has an intermediate behavior, probably due to the beneficial effect of the multilayer configuration and the more regular interdiffusion of Iron inside the ALD coating during the deposition process.
Polarization curves for the different samples are shown in Fig. 93. Uncoated AISI 316 L clearly shows a passive behavior in the 9 g/l NaCl solution, with a corrosion current density between $10^{-6}$ and $10^{-7}$ A/cm$^2$ and a passive region from 0.1 to 0.4 V with respect to Ag/AgCl. The Open Circuit Potential (OCP) for uncoated AISI 316 L steel resulted to be about 0.1 V with respect to Ag/AgCl.

All three ALD coated samples showed a negative shift of the OCP to about 0 V respect to Ag/AgCl for the Crystalline/Amorphous sample, to about -0.2 V respect to Ag/AgCl for the Amorphous/Crystalline sample and to about -0.3 V respect to Ag/AgCl. Both 2 layers coated samples clearly showed a reduction of the Corrosion Current Density to less than $10^{-8}$ A/cm$^2$. The Crystalline/Amorphous sample also showed a really limited passive region from 0.1 to 0.2 V respect to Ag/AgCl followed by a relatively fast increase of current density up to about 0.7 V, where pitting phenomena are triggered on the surface. The Amorphous/Crystalline sample shows a passive region from -0.2 to about 0.4 V respect to Ag/AgCl. The multilayer sample showed a stronger corrosion current density reduction, to less than $10^{-9}$ A/cm$^2$ with a wide passive region of about 1.6 V and a shift of the breakdown potential to about 1.4 V respect to Ag/AgCl.

The protective properties against localized corrosion of the stainless steel are clearly proved by the polarization curves and seem to be dependent on the characteristics and structure of the ALD coatings, as the three layers configuration proved to be more effective against corrosion compared to the two layer configurations, in particular reducing the corrosion current density of more than one order of magnitude and increasing the passive range of more than 1 V respect to the configurations based on only two layers.
The slightly worse behavior of the Crystalline/Amorphous coated sample could be related to the lower adhesion of the coating to the substrate, which may easily lead to a contact between aggressive media and samples substrate.
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8- CONCLUSIONS

A wide array of different ceramic coating deposits based on Al$_2$O$_3$ and TiO$_2$ were made on AISI 316 L substrates, in order to improve the already high corrosion resistance of this biomedical steel in biological solutions.

Due to the extremely low thickness of most deposits, the characterization of ALD coatings by conventional meanings were complex and in some specific cases incomplete characterizations had to be performed. Nevertheless, from the data acquire on the different experimental settings, the following general conclusions can be made:

- ALD can be successfully deposited on AISI 316 L stainless steel. No deposition defects, irregularities and/or variability in coating thickness could be observed on the whole coated surface. The ALD coatings resulted to be completely uniform and homogeneous even at critical locations such as sample edges and narrow crevices;
- SEM resolution and the transparency of thin ALD layers to the Ion Beam strongly reduced the possible use of this instrument for the characterization of the different layers, in particular for coating thicknesses under 100 nm;
- ALD deposition also proved to be not influenced by the surface roughness of the sample, as both coverage and corrosion protection resulted to be almost constant for both 2D and 2B cold-rolled steel standard finishings. AFM images were also successfully used to verify the integrity of the deposited ALD layers;
- AFM analyses at the interface between coated and uncoated regions resulted to be a reliable instrument to measure the coating overall thickness, even if the sharpness of the interface and the overall coating value resulted to be influenced by the substrate roughness for the 10 nm thick coatings;
- SKP-FM measurements
- Vickers adhesion tests proved to be a simple and reliable investigation method to confront the adhesion characteristics of different ALD depositions, even if the delaminated regions could not be resolved in the case of 10 nm thick coatings due to the resolution limits of the SEM;
- Vickers adhesion tests clearly demonstrated that thinner ALD layers have an higher resistance to delamination when compared to thicker layers of the same composition. TiO$_2$, in particular, clearly showed worse adhesion to the substrate than Al$_2$O$_3$. Multilayer configurations of alternate composition proved to be useful in strongly reducing the delaminated area compared to single layer ones;
- Polarization Curves clearly showed that thicker ALD coatings have higher corrosion resistance with the same composition, even if corrosion resistance can be further improved applying multilayer configurations in substitution of single layer coatings;

From the previous observations it can be concluded that ALD is adequate for the corrosion protection of AISI 316 L stainless steel. In order to reduce the costs related to the long deposition processes required to obtain a coating thickness of 100 nm or more, thinner multilayer configurations can be applied, with the advantage of a better resistance to delamination.
The positive effects of multilayer configurations were also observed when layers of Al₂O₃ were deposited at different deposition temperature, in particular when amorphous Al₂O₃ was used as the first layer. Multilayer configurations obtained using Al₂O₃ deposited at the alternate temperatures of 120 and 300 °C showed higher resistance to delamination and higher corrosion resistance when compared to coatings with similar thicknesses.
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