



**Politecnico  
di Torino**

**ScuDo**

Scuola di Dottorato ~ Doctoral School

WHAT YOU ARE, TAKES YOU FAR

Doctoral Dissertation  
Doctoral Program in Materials Science and Technology (37<sup>th</sup> Cycle)

# **Electrochemical surface treatments for resorbable and permanent biomedical implants**

By

**Davide Pupillo**

\* \* \* \* \*

## **Supervisor(s):**

Prof. Sabrina GRASSINI, Supervisor

Prof. Francesco DI FRANCO, Co-Supervisor

## **Doctoral Examination Committee:**

Prof. Andrea BRENNI, Referee, Polytechnic of Milan, Italy

Prof. Michele FEDEL, Referee, University of Trento, Italy

Prof. Giulio MALUCELLI, Polytechnic of Turin, Italy

Prof. Luigi CALABRESE, University of Messina, Italy

Prof. Maria Vittoria DIAMANTI, Polytechnic of Milan, Italy

Politecnico di Torino  
2025

# Summary

Biomaterials are usually defined as materials used in contact with living body to treat or replace any tissue, organ or function in the body. The most important requirement of a biomaterials is the biocompatibility, i.e. they must perform with a specific application without disruption of normal body function. Nowadays, biomaterials are made of metal alloys, ceramics, polymers and their composites. Metallic implants were used as orthopaedic devices for temporary applications (e.g. plate, screw and pins) and permanent ones (e.g. joints). More recently, innovative metallic biomaterials have been used for the reconstruction of both hard and soft tissues using for example NiTi alloys, as shape-memory materials used for cardiovascular stent, and biodegradable metals for bone tissue regeneration. The selection of the metal is related to the specific medical application and can be divided in metals for permanent prosthesis and metals for biodegradable prosthesis. Metals used to realize permanent prostheses are required to stay in the host for a long time, so must be durable and reliable (e.g. stainless steels, Co–Cr alloys, Ti alloys). Metals used to realize biodegradable prosthesis are proposed to replace permanent biomaterials if implants are required to stay in the human body only for the time of tissue healing, avoiding secondary surgery (e.g. magnesium and its alloys, pure iron, and zinc and its alloy).

Key properties of metallic implants such as their corrosion resistance, their biocompatibility, their osteointegration ability, their antibacterial properties are strongly affected by their surface composition and features. The latter can be finely tailored by surface treatments, that can change not only the structure and morphology of the implants surface but can also allow to grow a functional coating. The challenge is to design surface treatments able to uniformly modify the metal or alloy surface, being cost-effective and easily scalable. In the light of the above, surface treatments carried out by electrochemical processes, such as anodizing and/or electroplating, are certainly particularly promising, since a correct selection of the process parameters (namely current density or potential, bath composition and temperature, etc.) allows to control the coating features.

The necessary surface modification depends on the kind of material. In the case of permanent implants, it is important to grant not only a good corrosion resistance over time, but also to promote osteointegration even in the presence of inflammatory conditions, and to have antibacterial properties. On the other hand, for biodegradable implants it is important to reach a very good control of the biodegradation rate, since the latter must match the healing process time. Notably, it is very important to hinder localized corrosion that can bring to local failure with detrimental effects for the implants. If we also consider the possibility to customize the implant for a specific patient using additive manufacturing techniques (e.g. laser powder bed fusion), it is also very important to control the surface finishing soon after the fabrication of the implants and to study the efficacy of the surface treatment

proposed for cast materials also for 3D printed components in spite their different microstructure.

This research project is focused on the design and test of surface treatments for both titanium- and zinc-based metals. For both materials, a careful study of their corrosion resistance in different simulated body environments was carried out to highlight their strengths and weaknesses. In the case of Ti alloys, several chemical and electrochemical surface treatments were carried out aimed at improving osteointegration without affecting corrosion resistance and to provide antibacterial properties, paying attention on the effect of inflammatory conditions on the implants. Surface functionalization was also carried out on 3D-printed biomedical plates with a special attention of polishing the surface left by the printing process.

In the case of pure zinc, we studied its corrosion resistance in different physiological solutions to understand limits and perspective of using this metal for biodegradable implants. The investigation started with a careful study of the corrosion resistance of zinc in different physiological environments in the attempt to better understand its behaviour not always clear due to some contradictory results reported in the literature. Then chemical conversion processes were carried out to tune the corrosion resistance of zinc with the goal to tune its biodegradation rate and reduce the initial ions release that can induce cytotoxicity. These investigations were carried out on both cast zinc and 3D-printed components to highlight (if any) the effect of this fabrication process.