THESIS ABSTRACT

Traditional endoprostheses are widely used to replace bone and articular surfaces in case of degenerative joint disease; however, the mechanical, biological and structural mismatches between bone and the implants may cause significant problems like failure or patient pain. Considering the increasing patients’ population with orthopedic implants, the clinical implication caused by corrosion of the biomedical implants must be considered very relevant for its serious consequences. Although the studies of corrosion and electrochemical behavior of CoCrMo alloys have reached a wide understanding of the phenomena involved, many aspects related both to the manufacturing processes and the biological environments to which they are exposed, are still unknown and need to be clarified to minimize the problems created by endoprosthetic implants.

Moreover, it is crucially important to design an implant, fully customizable and scalable, with an optimum combination of properties and geometries. In fact, the worse clinical outcomes are observed in post-traumatic patients, where the limited availability of prosthesis size and shape and the difference between the bone and implant stiffness further reduces osteointegration due to the stress concentration and shielding. The introduction of selective laser melting (SLM) technique offers a great potential in the fabrication customized implants through the consolidation of layer-by-layer metal powders. Although selective laser melted bioimplants may provide structures closer to the host bone, the rapid melting/cooling process, resulting in non-equilibrium microstructures, may change the corrosion and mechanical properties and affect structural integrity.

Several aspects concerning the effect of different SLM process parameters and different simulated body fluids (SBF) on the behavior of SLM CoCrMo samples are studied within this Ph.D. work, including:

- Microstructural characterization of CoCrMo alloys fabricated with different SLM process parameters
- Corrosion and electrochemical behaviour of the SLM CoCrMo alloys exposed to the different SBF also reproducing inflammatory conditions.

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- Comparison of the conventional CoCrMo alloys properties with those of SLM fabricated ones.
- Effect of SLM process parameters on the mechanical behaviour of these materials compared to those of wrought CoCrMo alloys.
- Effect of the post-processing heat treatment on the microstructure and corrosion behaviour in SBF of SLM fabricated CoCrMo alloys.

Within this thesis, 4 different types of samples were fabricated by SLM technique using different set of laser parameters. To address the above-mentioned points, the bulk and surface microstructural changes, induced by selective laser melting process, are investigated using X-ray diffraction (XRD) and a combination of different (post) microscopical characterization techniques: optical microscopy (OM), scanning electron microscopy (SEM) coupled with energy dispersive X-Ray spectroscopy (EDX) and Focused Ion Beam (FIB) technique. Moreover, to provide an in-depth investigation on the surface film nature and characteristics of the studied CoCrMo alloys, also Transmission Electron Microscopy (TEM), and Atomic Force Microscopy (AFM) are used. The corrosion and electrochemical behaviour are studied by polarization curves (PC), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) techniques during the exposure to SBF both in the presence and in the absence of simulated inflammatory conditions. In order to understand the effect of SLM process on mechanical behaviour and for exploring the mutual effect of electrochemical and mechanical processes on the alloy behavior, mechanical methods such as Vickers microhardness (VH), tensile and slow strain rate tests (SSRT) were utilized.

The main results of this Ph.D. work are classified into four types of experimental studies, each discussing the microstructural changes and the corresponding corrosion mechanisms comprehensively. The first study aimed at exploring the microstructure evolution and

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characteristics of CoCrMo alloys manufactured by selective laser melting. Both SLM alloys and their wrought (WRO) counterparts were examined using different characterization techniques.

The results of this work demonstrate that the rapid melting and cooling induced non-equilibrium microstructure in the SLM built samples, consisting of cellular dendritic structures. The samples showed a fine microstructure, characterized by Mo enrichment at the cell boundaries. On the contrary, wrought CoCrMo alloy showed a typical fine-grained monophasic FCC structure. The second study addressed the corrosion and electrochemical behaviour of the SLM alloys in controlled Phosphate-buffered saline (PBS) solutions in the presence and in the absence of inflammatory conditions. The results of this work lead to the better understanding of the effect of SLM process parameters on the corrosion properties of the alloys. The materials fabricated with SLM technology seem to be quite promising in terms of corrosion resistance, even in the presence of inflammatory condition, simulated with the addition of H_2O_2, but the corrosion behavior was found to depend appreciably on the alloy microstructure. Samples with finer microstructure showed a better corrosion behaviour, due to the uniform distribution of alloying elements and less Mo micro-segregations.

The alloys studied showed excellent corrosion resistance connected to the barrier properties of the passive film, mainly attributed to the protective capacity of Cr_2O_3. In the presence of inflammatory conditions, a lower corrosion resistance was observed in all the materials studied compared to that measured at pH= 7.4 and at pH= 4.

The studied alloys showed quite similar behaviour at pH= 7.4 and pH= 4 suggesting comparable barrier properties of the passive film, mainly ascribed to the protective capability of Cr_2O_3, reinforced by the presence of MoO_2. In the presence of inflammation conditions, the lower corrosion resistance was observed in all studied materials.

Following this, the third study focuses on the determination of the effect of the SLM process parameters on the mechanical properties of the studied alloys. The results reveal that the SLM

process can build parts with mechanical properties comparable with traditional wrought CoCrMo alloy.

Eventually, the fourth study investigated the correlation between the SLM process parameters and heat treatments on the microstructural characteristics and corrosion behaviour of the fabricated CoCrMo alloys. Finer cellular structure was found in sample fabricated with lower laser power. Heat treatment at 850°C for 180 min induced a progressive modification of the cellular structure, that broke down into fine and homogeneously dispersed globular particles. Electrochemical tests showed an overall good corrosion resistance of the as-built SLM alloys, comparable or higher than those of conventional wrought alloy. Heat treatment processes remarkably increase the corrosion resistance of sample fabricated with lower laser power. This result is probably connected to the formation of finer precipitates and more uniform distribution of particles.

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