SURFACE MODIFICATION OF METALLIC BIOMATERIALS USED AS MEDICAL IMPLANTS AND PROSTHESES

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Abstract: In this work some of the challenges and different approaches regarding biocompatible materials used as medical implants, are presented. The rapid integration, biocompatibility and endurance of medical implants are influenced by the surface characteristics of the replacement part. Different surface treatments can be used to alter the surface characteristics of medical devices. Surface chemistry and topography are two key factors regarding the adhesion of proteins and cells, and thus, specific surface features would influence the growth and proliferation of cells. Herein, a few surface modification techniques, which can be applied to medical implants and prostheses, are presented.

Key words: medical implants, chemical etching, biomachining.

1. Introduction

In the recent years, the development of metallic materials used as implants was driven by multiple technologies which could potentially offer the optimal properties for the successful application of implantable devices. The wide area of biomedical material contains important applications, such as, cardiovascular devices, prostheses, and dental implants [1]. One of the areas where improvements could be made, considering that the contact between the biological medium and the implant is made at its surface, is to change the surface parameters of the material, for better bioperformance. T. Hanawa [8] reported the evolution of surface modification techniques which could be applied to improve the biocompatibility of materials. Firstly, the evolution started from the mechanical modification of the surface (grinding), then it was focused on the morphological alteration (blast, groove, etching), physicochemical active surface treatments (chemical treatment and hydroxyapatite coating), biochemical active surface treatments (immobilization of biofunctional molecules), reaching finally to the research on modifying the biological surface in which the emphasis is put on the coating with stem cells and tissues [8]. The schematic for some of these surface modification techniques can be observed in Figure 1.

For adequate implant biomedical performance it is necessary to study the surface properties of the base material and

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improve them through different surface treatments (for example microabrasion, chemical etching, and microbial biomachining, among others). The main purpose of these techniques, which have been employed over the last decade, is to produce new microrough material surfaces in order to reach nanotopography features which could offer improved bio-performance [20].

For example, in order to minimize implant related infections, approaches have been aimed to reduce the rates of microbial attachment to the material surface. The second requirement for this treatment, apart from reducing the attachment rate, is to not compromise the function of the implant, followed by decreased toxicity.

It is well to know that the interdependence of surface chemistry and physical attributes can affect cellular behavior by enhancing cell adhesion and proliferation. The modification of the surface chemistry, which, in turn, influences the hydrophilicity, surface charge and wettability, is another important approach for developing new biomaterial implant surfaces [20].

When a surface modification treatment is applied, the material that will be in contact with the biological medium requires certain characteristics, such as adhesion to soft tissue, blood compatibility, inhibition of biofilm formation, bone formation, bone bonding, and in the same time leaving the bulk material mechanical properties intact (strength, toughness, durability, elasticity) [8], [18].

2. Basic Aspects of Surface Modification Methods for Metallic Biomaterials

The materials that are stronger, lighter, smaller and more complex, with an enhanced bioactivity profile and highly controlled biodegradation kinetics represent the main aim in development of biocompatible materials design. Furthermore, the materials with a minimum content of potentially toxic elements are definitely the most picked in the field of biomaterials [14].

If there are materials that already exhibit adequate bulk properties, their surface could be modified, even in the case of commercially available products, by mechanical, chemical, and physical methods or by a combination of the above techniques. Hereinafter, some surface modification techniques will be presented, with emphasis on the procedure steps and materials, followed by some reported effects.

2.1. Microabrasion

By cleaning or making the surface rough through mechanical modifications it will be possible to improve adhesion in bonding, thanks to the roughness of the structure which could offer a better biominalization [7].

Machining, polishing, and grit-blasting are some of the mechanical surface modifications which involve physical treatments, such as shaping or removing the materials surface [15]. Microabrasion involves modifying the surface roughness
with the employment between the interacting surfaces of hard particles, smaller than 10 μm [17].

Figure 2 represents a schematic diagram of the mechanism of microabrasion. In this particular case, a 25 mm diameter ball is in a rotation motion on a stationary sample (the material that needs to be surface treated). The ball is held between two-coaxial shafts, each carried by a support bearing. To deliver the slurry solution (which contains the micro particles) on the contact area, it is used a variable speed DC motor. The L-shaped arm is rotated around its pivot until the sample becomes in contact with the ball. The beam is in balance when the ball and material surface are in contact, and the load is applied by adding dead weights to a cantilever arm [17]. In this way the microabrasion parameters can be strictly controlled.

Fig. 2. Mechanism of microabrasion [17]

Microabrasion is important due to the following: being directly related to the mechanisms of the wear process in biotribological applications it has widespread applications in conditions used in the space and offshore industries, to bio-engineering for artificial joints and implants [17], [23].

2.2. Chemical Etching

Chemical methods are used for improving biocompatibility, bioactivity and bone conductivity, corrosion resistance and removal of contamination. These methods offer to biomaterials bioactive surface characteristics. The most widely used chemical methods are chemical etching, acid and alkaline etching, electrochemical anodization, chemical deposition and biochemical surface coating [9], [15], [16], [19].

The objective of chemical etching is to remove one phase from the surface material and leave another unaffected. Furthermore it can be anisotropic which means removing material at the bottom of a trench and leaving the sidewalls unaffected [2], [4], [6].

Pure chemical etching, of which the schematic is presented in Figure 3, is an isotropic process because the gas phase neutral etchant atoms or molecules approach the substrate with near uniform angular-distribution. Large etching rates characterize pure chemical etching, and not anisotropic etching. Higher fluxes of active chemicals instead of fluxes of ions from the etching plasma discharge causes large etching rates [6].

As an example of the materials and procedures for this type of surface treatment, hereinafter we will present some information collected from the literature. It was reported in Ref. [22] that the roughness of a material is modified using the following protocol: on the sample surface a solution of 20 mL hydrogen chloride, 10 mL nitric acid and 3 g ferric chloride...
chloride is placed for 3 min and, afterwards, the surface was ultrasonically cleaned in distilled water for 3 min. As expected, changing the solution concentration, the proportion of the components, and etching time will influence the end result.

2.3. Biomaching

Generally speaking, machining is a process which removes a material from the bulk or surface material, while the remaining material will have the desired shape and dimension [5]. There are two categories in which one could classify the various machining techniques that are used nowadays, as presented hereinafter: chemical (the removal of material through chemical means) and physical (the removal of material through physical means) processing [10].

Micromachining, and in particular biomachining, represents a controlled microbiological process to selectively form microstructures on a metal workpiece by metal removal using micro-organisms [10], [11], [13]. The most promising microorganisms used for biomachining (such as Thiobacillus Acidithiobacillus ferrooxidans (At. Ferrooxidans)) are able to oxidize and reduce metals as part of their energy production cycle [5], [11].

The development of these microorganisms used for medical devices involves multiple physicochemical and biological parameters depending on the properties of the micro-organisms and of the materials [21].

The basic schematic of the biomachining mechanism is illustrated in Figure 4. In this particular case, the attachment process of bacteria on a copper surface is mediated by extracellular polymeric substances surrounding the bacteria [3], [20]. In the following section the influence of the initial surface characteristics and biomachining period will be presented.

Istiyanto et al [21] reported two cases of biomachining, using the following protocols: 800-grit and 220-grit initially polished samples were each biomachined for 6, 12 and 18 hours, respectively. On the 800-grit samples, before machining, a linear pattern was noticed on the surface, as a consequence of the polishing process. After machining the linear pattern disappeared, and it was replaced by a random pattern. In this first experiment, the average roughness ($R_a$) had an initial value of about 0.4 μm. After 6 hours of biomachining, $R_a$ increased to 0.6 μm. After 12 hours $R_a$ was changed to 0.8 μm. The most important phenomenon occurred after 18 hours of machining, after which a sudden increase of $R_a$ was noticed, from 0.8 (for 12 h) to 1.7 μm.

The second experiment, in which the samples were initially polished with 220 grit sandpaper, had similar results after the machining, when compared to the 800-grit samples. Therefore, after 6 hours $R_a$ was changed to 0.6 μm, after 12 hours $R_a$ was increased at 0.7 μm, and finally after 18 hours the roughness was increased to approximately 1.6 μm. This means that a similar rise in roughness was observed after 18 hours. Furthermore, it was reported that the enhancement of the cell viability and antibacterial effects has been
achieved by surface modifications, followed by the formations of new functional groups on the surface [21].

The main disadvantage of biomachining is represented by the very slow growth of chemolithotrophic bacteria; this means that the biomachining rate could be slightly reduced in comparison with the established chemical machining process [15].

3. Conclusions

A few surface modification techniques, which could potentially be used in biomedical applications, were presented. The interactions among materials surfaces and different tissues must be properly understood because this knowledge is essential in order to develop new materials.

Despite some outstanding properties that biomaterials have, since they are bioinert, materials surface modification is necessary to improve osseointegration, haemocompatibility or other properties related to biomedical applications. As biotechnology is developed, the application of microorganisms in material processing has been used more often.

In order to improve the performance of biological techniques for material processing it is necessary to compare the properties of both the natural and modified surfaces, through the investigation of physical, chemical and biological parameters using a standardized and structured approach.

An effective way for generating novel patterns needed for medical applications is made possible by combining two or more types of surface treatments. This allows to create new possibilities in fabricating more complex three-dimensional microstructures on biocompatible materials.

References