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METALLIC BIOMATERIALS: STAINLESS STEEL, TITANIUM AND ITS ALLOYS, AND COBALT-BASED ALLOYS

BIOMATERIAS METÁLICOS: AÇO INOXIDÁVEL, TITÂNIO E SUAS LIGAS E LIGAS BASEADAS EM COBALTO

BIOMATERIALES METÁLICOS: ACERO INOXIDABLE, TITANIO Y SUS ALEACIONES, Y ALEACIONES A BASE DE COBALTO

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ABSTRACT
Metallic biomaterials have extensive uses and applications in medicine, primarily in bone replacements and repairs, metal plates for fractures, and dental implants, as well as tissue replacement. The use of metals in biomaterials provides greater corrosion resistance, mechanical strength, and biocompatibility. The main metallic biomaterials are stainless steel, cobalt-based alloys, and titanium and its alloys. The objective of this work was to study the properties that allow these metals to be used in biomedicine, where the performance of each metallic biomaterial was assessed, as well as their properties. The importance of different metallic alloys and their properties was also highlighted.

Keywords: Metallic Biomaterials. Biomedicine. Stainless Steel. Titanium.

RESUMO
Os biomateriais metálicos possuem grande utilidade e aplicação na medicina, sendo utilizados principalmente em substituições e reparações de ossos, placas metálicas para fraturas e implantes dentários, como também na reposição de tecidos. A utilização de metais nos biomateriais permite maior resistência a corrosão, resistência mecânica e biocompatibilidade, sendo os principais biomateriais metálicos aço inoxidável, ligas baseadas no Cobalto e titânio e suas ligas. O objetivo deste trabalho foi um estudo sobre as propriedades que permitem tais metais serem utilizados na biomedicina, onde verificou-se a atuação de cada biomaterial metálico, assim como as suas propriedades. A importância de diferentes ligas metálicas e suas propriedades também foram evidenciadas.

Palavras-chave: Biomateriais Metálicos. Biomedicina. Aço Inoxidável. Titânio.

RESUMEN
Los biomateriales metálicos tienen amplios usos y aplicaciones en medicina, principalmente en reemplazos y reparaciones óseas, placas metálicas para fracturas e implantes dentales, así como en el reemplazo de tejidos. El uso de metales en biomateriales proporciona mayor resistencia a la corrosión, resistencia mecánica y biocompatibilidad. Los principales

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biomateriales metálicos son el acero inoxidable, las aleaciones a base de cobalto y el titanio y sus aleaciones. El objetivo de este trabajo fue estudiar las propiedades que permiten el uso de estos metales en biomedicina, evaluando el rendimiento de cada biomaterial metálico y sus propiedades. También se destacó la importancia de las diferentes aleaciones metálicas y sus propiedades.

Palabras clave: Biomateriales Metálicos. Biomedicina. Acero Inoxidable. Titanio.

1 INTRODUCTION

Biomaterials began to be used in medicine thousands of years ago, more specifically in sutures. However, in the middle of the twentieth century, after World War II, doctors found that ex-combatants wounded with some types of projectiles had a lower reaction to the foreign body (metallic), intense research began with the discovery of the beneficial action in the use of metallic materials as biomaterials.

From these discoveries, it was possible to use metallic biomaterials in various areas of medicine, biomedicine and dentistry. Implants, metal plates for fractures and tissue replacement are some of the various applications of metal biomaterials. The biocompatibility of metals is one of the main factors of their use.

In addition to biocompatibility, there are also properties such as mechanical strength, corrosion resistance and wear resistance. The main metals that have such properties are: stainless steel, alloys based on cobalt (Co) and titanium (Ti) and their alloys [1]. Despite the wide use of metallic biomaterials in the health area, there are still studies focused on this area, aiming to minimize some problems that can still be generated by metals, such as the release of metal ions that can sometimes be harmful to health [1,2].

There are several researches in metallic biomaterials, aiming to highlight each metal and its properties. Allowing for greater development in this area.

2 DISCUSSION

The definition of biomaterials is: Any substance (other than a drug) or combination of synthetic or natural substances in origin, that can be used for a period of time, in whole or in part, as part of a system that treats, augments, or replaces any tissue, organ, or function of the body

In addition to being biocompatible, a biomaterial must be bifunctional. Biofunctionality is the set of properties that gives a given device the ability to perform a desired function, for the necessary time, which can be long, in the case of permanent implant, or short, in the case of temporary implant. It is related to the mechanical, physical, chemical and biological properties that allow the implant to perform its function [3].

Metallic materials are often used as biomaterials to replace structural components of the human body, because when compared to polymeric and ceramic materials, they have superior mechanical properties. Among the metallic biomaterials, stainless steels, cobalt-chromium alloys, commercially pure titanium and its alloys are the most used[4-7].

3 STAINLESS STEEL

Stainless steels are characterized by superior corrosion resistance to other steels and are classified into three categories according to their microstructure: ferritic, martensitic and austenitic. Among the stainless steels, the austenitic steel (non-magnetic phase-centered cubic crystal structure) stands out, which has chromium (16-18% by weight) and nickel (12-15% by weight) in its composition, which are responsible, respectively, for increasing corrosion resistance and ensuring the stability of the austenite phase [8].

Stainless steel among the metals is the most used by the Unified Health System SUS, as it reasonably meets the requirements of biocompatibility and resistance to corrosion in body fluid. For this reason and for its mechanical property and low effective cost when compared to other metallic implant materials, stainless steel is the most frequently used biomaterial for internal fixation of devices.

Stainless steel, as its name implies, has elements that allow it to be resistant to oxidation, that is, high defense against corrosion. Molybdenum, for example, improves corrosion resistance in salt-containing liquids, while nickel allows the stabilization of the austenitic phase at room temperature, in addition to also increasing corrosion resistance, such as chromium [9].

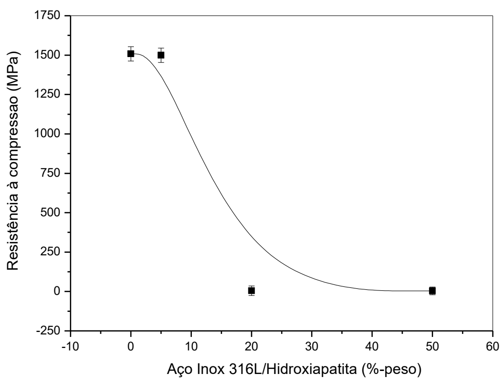
According to the interfacial response caused by the biological interactions between the implant material and the recipient tissue, stainless steels are classified as relatively inert materials, as they do not form a chemical bond with bone, being fixed to the biological tissue only by morphological fixation. When implanted, a capsule of fibrous tissue occurs around the implant of varying thickness, which depending on the amount of relative movement can lead to deterioration of the functions of the implant or the tissue at the interface. In addition to this lack of bone interaction with the implanted material, the elastic modulus of stainless steel and bone has a great difference, which causes bone degeneration over time, impairing the patient's rehabilitation.

However, the cost of producing this biomaterial is still one of the lowest today, which is why it is widely used as a bone replacement prosthesis. In the case of 316L stainless steel, an alternative to improve the response at the tissue-implant interface is the development of 316L stainless steel biocomposites with a bioactive material, such as hydroxyapatite (HA, Ca10(PO4)6(OH)2)). Due to the chemical similarity of hydroxyapatite with the mineral phase of bone tissues, it has good biocompatibility and bioactivity [10]. However, HA has low mechanical resistance that makes it impossible to use it to replace structural components in the human body [11]. Several studies are being carried out with biomaterial composites to unite the properties of mechanical strength and bioactivity.

Recently, the biocomposite Inox-HA was studied, using mixtures of 5%, 20% and 50% HA in a 316L stainless steel matrix, homogenized in a planetary ball mill with an inert atmosphere, where the values of compressive strength for the concentration of 5% was close to the stainless steel without HA (1500 MPa) while for the concentration of 20% there was a great decrease in the compressive strength (4.9MPa), thus making its use as a structural component in the human body unfeasible, Figure 1.

Figure 1

Compressive strength



Despite having the aforementioned properties, 316L stainless steel can still suffer corrosion inside the human body in some circumstances, such as high stress and high oxygen content. For this reason, this type of metallic biomaterial is more used in temporary devices such as fracture plates and temporary prostheses.

4 COBALT-BASED ALLOYS (Co)

They are usually known as cobalt-chromium alloy. In the manufacture of implants, two types of alloy are mainly used: CoNiCrMo and CoCrMo. The prostheses produced by these alloys have high resistance to wear, they are often used as hip and knee replacements. In its composition, the addition of Molybdenum allows obtaining a material with smaller grain sizes, which improves its mechanical resistance after forging or casting [1].

The first type of alloy mentioned is the most used among the cobalt-based alloys, as it has high resistance to seawater and cold work in this alloy can increase mechanical resistance. They also have high fatigue resistance and stress resistance, making the material useful in long-term appliances [1].

It can also be used as a conventional metal structure of the removable partial prosthesis, made with Co-Cr-Mo alloy, however it may encounter obstacles to its adaptation and retention. One of the problems is the lack of flexibility of the holding arm. If the retentive arms of the clamps are made of gold alloy, the problem can be solved, since this alloy is more flexible than Co-Cr-Mo. The **CoCrMo alloy (F1537),** the ASTM **F1537** - Standard Specification for Wrought Cobalt-28Chromium-6Molybdenum Alloys for Surgical Implants is the alloy used to replace knee prostheses [12], highly resistant to wear figure 2.

Figure 2

Knee prosthesis (Sandnox Biometais) Nitinol

The term Nitinol designates a set of alloys of Ni (Nickel) and Ti (Titanium) that have the property of "shape memory effect". A nitinol object at room temperature is easy to warp, but after apparent deformation, it becomes rigid and regains its original shape when heated above a certain temperature. It is a phase change in the solid state (austenite/martensite). Nitinol alloys have 48-60%Ni and the remainder of Ti.

Nitinol was discovered in the 1960s at the U.S. Naval Ordnance Laboratory (NOL, located in White Oak, Maryland). The name of the Nitinol alloy is composed of the chemical symbols of the elements (Ni, Ti) along with the laboratory acronym (NOL). F2063 Nitinol, Nitinol Wire, Nickel Titanium Wire and F2063 Wire are the materials that have excellent biocompatibility, that is, compatibility with organic tissues. For this reason, Nitinol F2063, Nitinol Wire, Nickel Titanium Wire and F2063 Wire have been widely used in bioengineering applications as material for heart valve tools, guide wires for catheterization, minimally invasive surgical instruments, hip implants, bone staples and skull plates. Figure 3 shows a device that uses Nitinol wire.

Figure 3

Device made of Nitinol wire

5 TITANIUM AND ITS ALLOYS

Titanium (Ti) is a transition element that has excellent physical properties, among which the high melting point (1668 ºC), the boiling point (3287 ºC), the low specific mass (4.54 g $^{cm-3}$) and the modulus of tensile strength (above 12.7x104 MPa) [13] stand out. Of these properties, the specific mass and the modulus of elasticity stand out. Because titanium's modulus of elasticity is much higher than that of other light metals, such as magnesium (Mg) and aluminum (Al), it competes with them for space structural and nano-aerospace applications [14], since its melting point is much higher. In addition, Ti can be used under temperatures of up to 426 ºC in air. Temperatures higher than this cause it to be weakened by the oxygen in the air, because titanium combines very easily with other elements, especially gases such as nitrogen and oxygen, which dissolve quickly in the liquid or solid metal above approximately 400 ºC, causing the loss of ductility of the latter.

Titanium exhibits allotropy [15]. At room temperature, it has a compact hexagonal crystal structure, called the alpha phase, which is stable up to 882 ºC. Above this temperature the structure changes to body-centered cubic, called the beta phase. Alpha titanium is pure titanium or titanium whose voltage is increased by the addition of small amounts of stabilizing elements of this phase, such as Al, Sn, Ni and Cu. Alloys in which this element has an alpha structure do not have their hardness increased with cooling, but have higher stress than commercial pure Ti. α-β alloys are Ti alloys with a partially α and partially β structure. Elements such as Mo, V, and Ta, when added to pure Ti at room temperature, tend to promote the presence of the β phase. An important alloy from an industrial point of view is Ti-6Al-4V, which contains 6% Al and 4% V and has two structural phases (about 50% α and 50% β). Another very important chemical property is the high resistance to corrosion. Ti and its alloys have excellent corrosion resistance in seawater and in aqueous chloride solutions. Most alloys are resistant to a wide variety of oxidizing media such as HNO3 and reducing agents such as HCl and H2SO4 when they are diluted. Titanium is also resistant to most organic acids.

Ti and its alloys have been adopted for the manufacture of various biomedical devices used in orthopedic and dental implants due to the strength/weight ratio of these materials, resistance to corrosion in organic media and their biocompatibility characteristics [16,17]. Among these applications, non-resorbable membranes and microplates for cranial and oral and maxillofacial reconstruction, respectively, as well as plates and screws for osteosynthesis, intramedullary nails, and hip and knee prostheses, stand out.

Several studies have shown the importance of developing new titanium alloys, free of aluminum and vanadium, for the manufacture of implantable biomedical devices, containing more tolerable binding elements, from the point of view of toxicity. In this sense, the development of new β-type titanium alloys containing the addition of niobium, tantalum and/or zirconium can contribute to improving the corrosion resistance and biocompatibility characteristics of these implantable biomedical devices. However, the selection of elements with good biocompatibility characteristics and with elastic modulus values close to the bone can contribute to accelerate the bone-integration process, as occurs in the case of titanium alloys containing Nb, Ta and/or Zr, in particular the Ti-35Nb-5Ta-7Zr alloy [19].

The high production costs of titanium-based materials have slowed down its use in biocompatible implants and prostheses. Aiming to reduce this cost, powder metallurgy began to be used, providing a material that was also porous [17].

Initially, the following titanium alloy was used: Ti-6Al-4V, developed for aerospace. It was later discovered that vanadium (V) has high cytotoxicity, and can even cause irritation in the respiratory system. Another attempt to adapt the alloy was the decrease in the modulus of elasticity, in an attempt to bring it closer to human bone, being able to simulate the tensions suffered by the bone. In any case, Ti-6Al-4V continues to be the most widely used metallic biomaterial among titanium alloys [18,19]. Depending on the degree of purity of the titanium, it is used in different regions of the human body, as shown in figures 4 to 7.

Figure 4

Titanium Grade 1 (Sandnox Biometais)

Figure 5

Titanium Grade 2 (Sandnox Biometais)

Figure 6

Grade 4 Titanium (Sandnox Biometais)

Figure 7

Titanium Aluminum Vanadium (Sandnox Biometais)

6 CONCLUSION

Metallic biomaterials are increasingly of interest to researchers, this is due to the fact that they have vast utility in the field of medicine. Studies on the properties of metallic materials are essential to understand their use and biocompatibility. This article studied the properties of the most widely used metallic biomaterials and their applications in the area of biomedicine. Highlighting 316L stainless steel, cobalt (Co) alloys and titanium and its alloys. The advent of new metal alloys allowed the expansion of metal biomaterials, enabling studies with greater scope and not only in the medicinal area, but also in the dental area. Current studies focus on research of different alloys, such as Nitinol and titanium alloys.

Metallic biomaterials are of great importance in the area of materials, their biocompatibility allows their use in biomedicine and, therefore, studies are carried out looking for better metal alloys, combined with their properties.

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