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Survey and challenges of dental metallic materials

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1. Introduction

Metallic materials have been used in dentistry for centuries because of their superior mechanical and biological qualities. This trend is especially pronounced in modern life. Alternative materials, such as ceramics, are gaining popularity, but metallic materials are expected to continue to play an essential role due to their functional qualities and proven strong clinical responses in dental applications (*Anusavice, 2012, Parida, 2012, Patel et al., 2012, Pilliar, 2009, Kohn et al., 1996*). In this regard, dental metallic materials must meet standards and attributes such as biocompatibility, non-toxicity, corrosion resistance, durability (long-term), adequate strength and toughness, and corresponding modulus of elasticity (*Niinomi et al., 2012, Prasad et al., 2017*).

Metallic materials used in dentistry are biocompatible materials that come into contact with human cells, tissues, or body fluids either temporarily or permanently. They are most typically used to repair or upgrade structural components of teeth, which are part of the human body, to compensate for damage caused by aging, illness, or accidents (*Schmalz, 2009)*.

Because of their outstanding mechanical qualities, metallic materials are widely utilized in dentistry for a variety of devices (*Hermawan et*

ABSTRACT

The classification of dental metallic biomaterials is illustrated in depth, with a focus on dental casting alloys. Methods for creating dental prostheses as well as manufacturing shape memory alloys (SMA) Ni-Ti alloys are briefly given. The effect of surface oxide films on metallic biomaterials in the human environment is considered. In order for metal implants to interact with the human body, they need to meet certain requirements.

> *al., 2011*). Attention should be paid to [Table 1](#page-1-0) and a gold removable partial denture sample (*Rebeka et al., 2022*), [Figure 1.](#page-1-1)

> When it comes to complicated constructions and restorations that are subjected to a harsh corrosive environment as well as significant weights in the human body, no other construction material can compete with metals. Metals' outstanding mechanical properties, such as high strength, hardness, and wear resistance, set them apart from other materials and render them indispensable in dental applications (*Manivasagam et al., 2001*).

> Metallic materials have considerable disadvantages. The main disadvantage is the mismatch between the modulus of elasticity of metals and solid human tissues (bones and teeth) (*Geetha et al., 2009, Teoh, 2000*). The other disadvantage is their susceptibility to corrosion when in contact with biofluids, and the release of metal ions with a potential cytotoxic effect, which may affect the occurrence of neurological disorders and/or other serious health problems ([Figure](#page-3-0) [2](#page-3-0)). Furthermore, for dental applications, undesirable metal properties include a high coefficient of thermal conductivity, high density (replacements are too heavy), low aesthetic value, and problematic workability. The fundamental purpose of developing biocompatible metallic materials is to ensure that implants function well in the human body without causing injury, as well as to extend patients' lifespans and quality of life.

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Table 1. Common metallic materials/alloys used in dental appliances

*316L and 444 are stainless steels.

The most frequently utilized metallic materials for replacing a specific part or function of the human organism that are physiologically acceptable and cost-effective are titanium and titanium alloys, which have good corrosion resistance, appropriate biocompatibility, and low stiffness, allowing for the best transmission of mechanical stresses from the implants to the bone. Another advantage is the creation of titanium dioxide $(TIO₂)$ on the surface of Ti, which possesses bioactive qualities that promote new bone growth. Cobalt-based alloys (e.g., Co-Cr-Mo) have excellent mechanical and biocompatible properties (*Stamenković et al.*, *2023*) whereas stainless steels (*Standard, I. S. O., 2007*) have recently been abandoned due to insufficient corrosion resistance and the effects of the body's hypersensitivity to nickel (Ni), which is released due to steel implant and body fluids interaction.

Implant corrosion occurs when the passive film formed on the surface of a metallic material is damaged by friction and/or micromovements, causing the metallic implant to come into direct contact with biofluids, resulting in material degradation and metal ion release. As a result, understanding the kind and concentration of components released from the surface of implant materials is critical for predicting and assessing their local and systemic effects on the body (*Manivasagam et al., 2010*).

Metal ions emitted can be harmful in certain amounts and cause a variety of health issues due to ion diffusion throughout the body. Therefore, to increase the characteristics and longevity of implants, it is important to develop a material with a low modulus of elasticity, high strength, and strong corrosion resistance. Because metallic biomaterials are frequently utilized to replace damaged solid tissues in the human body, extra caution should be exercised when investigating their qualities, particularly their biocompatibility. As a result, the primary goal of developing metallic biomaterials is to improve their mechanical properties while also reducing corrosion damage and improving biocompatibility, which necessitates modifying the chemical composition, microstructure, and surface condition of metallic materials (*Schmalz and Arenholt-Bindslev, 2009, Prasad et al., 2017*).

2. Types of dental alloys

The global market is supplied with hundreds of various dental alloys, which can be classified based on the primary metal and alloying elements, [Table 2,](#page-1-2) as well as their application in dentistry, [Table 3.](#page-1-3) There is a more complete classification of casting alloys, provided in [Table](#page-2-0) [4](#page-2-0), used in metal ceramic prostheses and partial dentures. Certainly, a different field of use might be the basis for a distinct classification of dental alloys (*Standard, I. S. O., 2007, Niinomi et al., 2012, Prasad et al., 2017, Slokar et al., 2017*)

In fixed prosthodontics, dental alloys are characterized both by function and by composition. When identifying an alloy by the elements it contains, the constituents are listed in decreasing order of composition, with the largest constituent listed first, followed by the second largest constituent, such as Au-Ag-Pt (Au 78 wt.%, Ag 12 wt.%, and Pt 10 wt.%). An exception to this rule is the identification of some alloys by elements that significantly influence physical properties, suggest potential biocompatibility concerns, or both, such as Au-Cu-Ag-Pd (Au 40 wt.%, Cu 7.5 wt.%, Ag 47%, and Pd 4 wt.%).

Table 2. Classes of dental alloys according to the basic metal and alloying elements.

Primary metal	Alloying elements
Au	Ag, Au, Cu, In, Pd, Pt, Zn
Pd	Ag, Pd, Ga, Cu
Ag	Ag, Pd
Co	Co, Cr, Mo, Fe, C, Si, Mn
Ni	Ni, Co, Cr, Mo, Fe, C, Be, Mn
Ti	Ti, O, N, C, Fe, H
Hg	Ag, Sn, Cu, Zn, Pd
Stainless steel	Fe, Cr, Ni

Table 3. Typical components of dental alloys

Table 4. Classification of casting alloys for metal ceramic prostheses and partial dentures

*Alloy Classification of the American Dental Association (ADA)

2.1. Dental Casting Alloys

Inlays, onlays, crowns, classic all-metal bridges, metal-ceramic bridges, resin-bonded bridges, endodontic posts, and removable partial denture frameworks are all made from cast metals (*Pilliar, 2009; Niinomi et al., 2012*). Casting alloys have desirable properties such as biocompatibility, ease of melting, casting, soldering, and polishing, low solidification shrinkage, low reactivity with mold material, good wear resistance, high strength and sag resistance (metal-ceramic alloys), and excellent tarnish and corrosion resistance. In general, typical categories 2 and 3 of gold alloys serve as reference points for measuring the performance of other castings. Refer to [Tables 5](#page-2-1) and [6](#page-2-2).

In contrast, all casting alloys used in the oral cavity must be biocompatible. The biological risks of base metal alloys, particularly nickel and beryllium, are controversial. These dangers could affect not only the patient, but also the dentist and technician due to continuous exposure (*Niinomi et al., 2012; Prasad et al., 2017*).

In 1927, four categories of gold alloys were identified based on dental function, with hardness (VHN) increasing from Type I to Type IV (*de Matos, et al., 2021, Anusavice, 2013, Asakura, 2012*) [Table 5.](#page-2-1) In 1989, the ADA's Specification No. 5 classified the four alloy types, as well as the fifth type, based on their qualities rather than their compositions, as shown in [Table 5](#page-2-1) (*de Matos, et al., 2021*).

Table 5. Four types of gold alloys

Table 6. Types of metal alloys and their main indications

Since 1989, any composition may be used in ADA-approved casting alloys as long as it passes the tests for toxicity, tarnish, yield strength, and percentage of elongation. The evaluations generate strength, and the amount of elongation varies according to the loads applied to the restorations.

It is obvious that there is no ideal dental alloy that is superior and irreplaceable, which is why there is a wide range of metallic materials with potential applications in dentistry.

Pure metals are rarely utilized in dental prostheses. For example, gold has a low hardness, but silver oxidizes. Therefore, pure metals cannot meet the rigorous demands placed on dental metal products. As a result, careful alloying is employed to produce the required combination of beneficial qualities. For example, alloying alters mechanical qualities, corrosion resistance, workability, color, and a variety of other important characteristics.

When casting dental alloys, the goal is to obtain a fine-grained microstructure with the least amount of chemical segregation. Dental alloys can be homogenous or heterogeneous based on their chemical composition and microstructure. Homogeneous dental alloys have the same physical and chemical properties throughout the volume, meaning they are made up of grains from a single phase. Heterogeneous dental alloys are made up of areas with varying physical and chemical properties, i.e., grains from distinct phases. These changes are accomplished through regular alloying and proper heat treatment (*Hermawan et al., 2011, de Matos et al., 2021*).

High strength, low modulus of elasticity, good corrosion resistance, and biocompatibility are desired characteristics of implant materials that are difficult to achieve at the same time, making material development for dental implants very complex and challenging. To obtain a material with optimal characteristics, various technological procedures are used (thermomechanical, chemical, electrochemical, surface modification, etc.), which improve the desired properties of the material while reducing or eliminating harmful properties. Modern intensive plastic deformation procedures have recently been used to produce fine-grained metal materials with improved mechanical properties when compared to materials produced using traditional manufacturing methods, though the question of their corrosion resistance and biocompatibility remains open (*Stamenković et al., 2023).* Given that metallic biomaterials are in long-term intimate contact with living tissues, it is possible to conclude that knowledge and understanding of the interactions between the implant material's surface and human tissues is extremely important for the development of new materials for use in medicine, and thus the material's non-toxicity and biocompatibility become critical factors in the further development of implant metallic materials (*Slokar et al., 2017; de Matos, et al., 2021; Anusavice, 2013; Asakura, 2012*)

3. Methods for creating dental prosthesis

The tooth restorations can be made via digital computer-aided design and computer-aided manufacturing (CAD/CAM) techniques, traditional lost wax precision casting, or a combination of these techniques. Today's society places a high value on aesthetics, so the metallic structures that are created are subsequently veneered with composites or ceramics. Due to their poor aesthetics and wear endurance, acrylics were once widely utilized but are either completely out of use now or are gradually becoming less so in various nations. While metal-free full ceramic restorations are aesthetically pleasing to the fullest degree, their poor strength and ductility make them unsuitable for long-spanning dental bridges or removable partial dentures. For these indications, metallicceramic restorations are thought to be the best choice.

One can categorize the digital CAD/CAM techniques into two groups: additive manufacturing and subtractive manufacturing. In subtractive manufacturing, a traditional metal cast is made after a block of dental alloy material or a plastic or wax blank disc is milled (a combination of digital and analog techniques). This allows for the creation of dental restorations. Selective Laser Melting (SLM) or Electron Beam Melting (EBM), the two most popular techniques for dental restorations, are typically utilized in additive manufacturing, also known as 3D printing. The process of creating tooth restorations using metal dental alloys is depicted in [Figure 2.](#page-3-0) Because CoCr dental alloys are accessible as solid disc blocks for milling, tiny cylinders for

casting, or powder for 3D printing, they are commonly employed in all of these processes. CoCr alloys are currently regarded as the preferred material for base-metal dental framework fabrication because of its accessibility in dental fabrication processes, clinical performance, affordability, biocompatibility, and mechanical qualities (*Presotto et al. 2021; Stamenković et al., 2023.*).

In order to create a wax model of a tooth restoration, the traditional lost wax casting method for prosthesis creation entails taking an impression of the patient's oral cavity, pouring a plaster mold of the oral cavity, investing the tooth restoration, casting the chosen metal, and polishing the finished prosthesis. Although this method is timeconsuming and sophisticated, it offers physicians an inexpensive choice (*Park et al., 2015*). The possibility of inaccuracy may increase during this operation, depending on the qualities of the material utilized and the worker's expertise. In order to improve on this fabrication, automated CAD/CAM technology was subsequently brought to the dentistry sector. This technology offers the potential for increased output, user-friendliness, time savings, and a decrease in the impact of laboratory variables and human error.

Due to their ability to produce dental prostheses quickly, precisely, and with less material waste than milling, additive manufacturing techniques are becoming more and more popular. The acceptance rate of these procedures in dentistry laboratories is rising as a result of the technologies' ongoing improvement, which makes them more accessible and user-friendly. The disruptive nature of additive

Fig. 2. Process flow for the various dental prosthesis manufacture methods, (*Rudolf et al., 2024*).

manufacturing makes it particularly well-suited for creating customized metal structures for dental prostheses, where each metal framework can be regarded as a unique product or a customized medical device meant only for the patient for whom it was intended.

3.1. Manufacturing methods for SMA Ni-Ti alloys

 SHS HIP

Similarly, for SMA Ni-Ti alloys, a brief explanation of production procedures is provided (*Laplanche et al., 2015; Mehta and Gupta, 2019)*. The majority of fabrication techniques are categorized as being listed in [Table 7](#page-4-0).

Table 7. Review of the processes used to manufacture SMA NiTi alioys.

Manufacturing of NiTi Components Casting Powder Metallurgy VAR VIM EBM Conventional Processes Additive Manufacturing

 $\stackrel{\text{II}}{\text{MIM}}$

LENS EBM

The two most commonly used melting procedures are vacuum arc remelting (VAR) and vacuum induction melting (VIM). Both of them supply appropriate SMA NiTi orthodontic wire material in compliance with ASTM F2063.

4. Oxide Film on Dental Alloys in the Human Environment

In this regard, it is worth noting that the surface oxide film generated on metallic materials acts as an inhibitor for the release of metallic ions, and the behavior of the surface oxide varies with ion release. Furthermore, the composition of the surface oxide layer changes due to reactions between metallic material surfaces and living tissues. Even low levels of dissolved oxygen, inorganic ions, proteins, and cells can stimulate metal ion release. The oxide coating that prevents metal ion dissolution is not always stable in the human body, so a thorough study of the oxide film's behavior in vivo is required to better understand the corrosion phenomenon (*Manivasagam et al., 2010; Rudolf et al., 2024*). [Table 8](#page-4-1) shows an overview of the surface oxide films on various metallic biomaterials.

When the surface oxide layer of a metallic substance is broken, corrosion occurs, and metal ions are constantly released unless the film is renewed. The interactions between the physiological medium and the metal determine how long it takes for the oxide layer to renew. The time required for repassivation, also known as regeneration time, varies depending on the alloy being used. The regeneration period, as indicated above (*Hanawa, 2003*), influences both the corrosion rate following disruption and the amount of metal ions released. [Table 9](#page-4-2) displays the regeneration time required to create surface oxide layers in various alloys.

Table 8. Overview of the surface oxides that can occur on various metallic biomaterials.

Table 9. Regeneration period of surface oxide coverings for certain alloys.

Based on these results, it was found that Ti-6Al-4V, a well-known alloy that is frequently used for orthopedic applications, has a shorter regeneration time than stainless steel. This suggests that stainless steel releases more metal ions than the latter, underscoring one of the alloy's superior qualities in addition to its other beneficial properties.

Numerous biological factors are impacted by the reactivity of metallic ions that leak out of the implant due to corrosion in the human body. When a material corrodes, metal dissolution produces erosion, which ultimately results in the implant becoming brittle and breaking. When a metal splits, the exposed surface area rises and the protective oxide covering is lost, which leads to increased corrosion. Inflammation of the surrounding tissues may result from the dissolution and further fragmentation of the metal fragments if they are not surgically removed (*Hanawa, 2003*). The possible risks associated with the corroded implant material are shown in [Table 10](#page-4-3).

Table 10. Effects of various metals on corrosion in the human body

Unwanted biological reactions in the host are likely caused by corrosion products and reported elevated levels of corroded particles in tissue around implants and other human body parts, including the kidney and liver. Meanwhile, the delayed release of metallic ions due to corrosion is not supported by histology evidence. However, it is evident from the darkening of the surrounding tissue and the foreign body reactions that implant corrosion is the cause of this (*Manivasagam et al., 2010; Hanawa, 2003*)

5. Requirements that metal implants need to fulfill

5.1. Interaction between metallic implant and human organism

Under normal conditions, body fluids consist of a 0.9% NaCl solution that contains proteins and amino acids. Body fluids comprise liquids like blood, lymph, and tissue fluids as well as solids such as leukocytes, macrophages, and blood particles including lymphocytes, platelets, and erythrocytes. Body fluids have a pH of 7, however under normal conditions, they can have a pH of 4-5 because of the emergence of inflammatory processes brought on by trauma or surgery, i.e., metabolism disorders. The body's fluids have a temperature of 37 °C and a pressure of 0.1 MPa, respectively. (*Aksakal, 2004; de Souza Costa et al., 2014*). For instance, the different types of biological tissues (epithelial, connective tissue, and alveolar bone) that come into contact with the Ti implant will dictate the optimum features of the implant's surface at a specific site ([Figure 3](#page-5-0)).

Fig. 3. The various biological tissue types in touch with the Ti implant include epithelium, connective tissue, and alveolar bone.

The biological milieu that is described for the human organism is extremely corrosive to metals. First of all, because of a lower partial pressure of oxygen in the human body than in the atmosphere, biocompatible metallic materials corrode more quickly, and hence the surface oxide layer that acts as a passivator takes longer to regenerate after being damaged or removed from the material (*Hanawa, 2003*).

The stress added to the material's fundamental stress during cyclic friction is what leads to the manifestation of material fatigue during friction. Friction fatigue occurs when the metallic implant is statically pressed on the surface of a cyclic stressed substrate, such as a bone. Small amplitude relative displacements on the contact surfaces of the two components cause friction, which decreases the oxide layer's compactness and permits the creation of a free metal surface on the implant's surface (*Aksakal et al., 2003*).

The human body experiences wear and tear due to the friction between metallic components, which constantly releases metal ions, metal compounds, and wear products (metal filings). All the metal products listed above have the potential to leak into the living tissues around medical implants, poisoning the affected area or organ (*Hu et al., 2010*). One example of this is the development of black tissue surrounding the implant, which is a sign of metallosis in clinical orthopaedics.

This shows that metallic materials encounter significant chemical and mechanical aggression in the human body, further compromising their durability and biocompatibility.

5.2. Requirements that have to be fulfilled

Medical implant materials need to fulfill the following crucial requirements:

• Compatibility with biological systems. Materials that are inserted into tissues need to have strong biocompatibility, or a strong cellular inclination toward the implant's surface. From a technical perspective, a wide range of materials are ideal for creating implants. But no matter how good its engineering is, if the tissue cannot accept the "foreign body," it is not suited for implant production (*Milenković et al., 2012, Rudolf et al., 2015*).

• Resistant to corrosion. Biocompatible metallic materials shouldn't corrode at all when in contact with living tissues (*Manivasagam et al., 2010*).

• Durability. When metallic materials are inserted into the human body as implants, they should not break down over the course of their operating time. This means that they should have high fatigue strength during corrosion and friction, as well as a slight particle release during wear and friction.

• Strength and toughness. Due to the restricted space in the human body, the implant's dimensions must be as compact as feasible, and its strength and toughness ratings must be high enough.

• Low modulus of elasticity. A highly unfavorable feature of biocompatible materials, which are used in orthopaedic surgery and dentistry today, is that their Young's moduli are five to ten times higher than the Young's modulus of a human bone (*Geetha et al., 2009*), [Figure 4](#page-5-1). This is because the elasticity difference between the metallic material and the bone, which are in contact, places a significant load on the bone and causes a decrease in bone density. To increase the implant's resistance to fatigue fracture, it must be made of alloys suited for precision vacuum casting, forging, and cold forming in addition to the necessary final mechanical processing. Implants typically have a complex configuration.

Elastic Modulus (GPa)

Fig. 4. Modulus of elasticity for the most prominent dental alloys, adapted from (*Geetha et al., 2009*).

Finally, the main three groups of features, presented in [Figure 5,](#page-6-0) summarize the overall requirements that the metallic implant needs to fulfill (*Kohn et al., 1996*): (i) Compatibility, (ii) Mechanical properties, and (iii) Manufacturing.

6. Conclusions

Understanding the fundamental characteristics of a dental alloy, such as its strength, hardness, and melting point, can help determine which alloy is the best choice for a given patient and application.

Fig. 5. A summary of all the requirements, adapted from (*Kohn et al., 1996*)

Consequently, dentists find it challenging to select the best material due to the wide variety available on the market. Therefore, they should adhere to the following guidelines: (i) it is imperative to have a thorough understanding of the alloy; (ii) it is necessary to ascertain the chemical composition of the alloy and to avoid any elements that may trigger a patient's undesirable reaction; (iii) single-phase alloys should be used whenever possible; (iv) only corrosion-resistant alloys, as demonstrated by investigations; (v) just materials that have been demonstrated to be effective and are made by reputable producers should be used; and (vi) finally, it is crucial that the dentist takes responsibility for the safety and effectiveness of any intervention.

Thankfully, advances in technology nowadays make it possible to produce alloys with better qualities and improved properties (*Niinomi et al., 2012; Prasad et al*. *2017).*

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