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Review paper

Short review on hydroxyapatite powder coating for SS 316L

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Abstract

Medical implants and other biomaterials are used by millions of individuals all over the globe to restore lost bodily functions due to injury or illness. Many of these implants fail after a short time or have difficulties, despite the fact that they play important roles in keeping a person's life safe or increasing the quality of their lives. It is the lack of biocompatibility that has proven to be the biggest downfall of biomaterials. Investments in this industry may be made using a thin film of hydroxyapatite powder (HAP) on stainless steel. Plates, screws, pins, and artificial joints are only some fixation devices for bones that often use 316L stainless steel. However, due to its unique advantageous qualities such as super-elasticity and low-profile feature, thin film HAP signals a high potential for use in compact new cardiac devices like the cardiovascular system and protecting stent grafts.

Keywords
Biomaterials; biocompatibility; implants; plasma spray; coatings

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Introduction

The bones, joints, and teeth that make up the human skeletal system may heal from a broad range of ailments with basic care. There has been a dramatic increase in the complexity of orthopedic injuries since the advent of industrialization. Orthopedic surgery may be necessary to repair or replace a broken bone. Above 500,000 joints are replaced each year in the USA alone, and thousands of patients have this procedure every year globally [1]. The average demand for complete implants is anticipated to rise by almost 30 % over the next decade and a half [2]. There will be an increase from 10.1 million to 13.9 million people living with osteoporosis between 2002 and 2020 [3]. As a result, Ti-based alloys, stainless steel, and alumina/zirconia ceramics have been the only biomaterials employed in these implants up to this point [4]. Bone cement, used for affixing joint prostheses, is a common component of such treatments. Bone cement is used to fill bone and dental cavities using self-curing polymers, and they also serve as load distributors for implants. Due to its bio-stability and high mechanical qualities, poly(methyl methacrylate) is used in this sector since the 1960s [5]. It is essential to mimic the composition and structure of genuine bone to achieve features comparable to those of natural bone. In order to do this, it is necessary to study the anatomy of real bone [6].

Coating is the technique used to improve the mechanical properties of a surface. This method is also used in biomedical applications where metal implants predominate. Despite the fact that metal devices offer beneficial features, including higher strength, corrosion-resistant, and biocompatible properties within the human body, they are nonetheless not without their drawbacks. These gadgets still used metal and were rusted in varying conditions. Because of its great stability and biocompatibility, hydroxyapatite (HAP) is often used as a coating for metal implants [7]. It is well-known that steel corrodes in moist settings like the human body. So, Babu *et al.* [8] use a dip-coating technique to attempt to improve the bioactive coating of implants. SS316L steel was used as a base material with HAP made of biphasic calcium phosphate for the experiments. Before anything else, specimens of the substrate were heated for 15 minutes in a solution containing 20 % of HNO_3 at 600 °C to create nonreactive substrate surfaces. Substrate specimens were then submerged in the HNO_3 based solution to start the coating. Results showed that utilizing this approach at the right temperatures will strengthen the adherence of the coating to the base material.

Many scientists have tried utilizing ceramic powders as additives to coating solutions to form a protective layer on metals since thermally treating metals to decrease corrosion is still insufficient. Choudhuri *et al.* [9] offered a novel method, cold spraying bio-ceramic coatings onto metals at temperatures below their melting points (metal melting point). The composite powders used in this research are composed of titanium and HAP, with a proportion of HAP as high as 30 %. The research also found that the ratio of HAP deposition to HAP in the coating solution decreased with time. The binding strength for the deposit was also similar to that of plasma-sprayed HAP. The electrophoretic deposition (EFD) often used in thin-film fabrication was used to apply HAP coatings on SS316L surfaces in an investigation by Fadli *et al.* [10]. Three different voltage impacts of 40, 50, and 60 V on the characteristics of the coating layer were investigated. Quantitative analysis of Ca and P in HAP coatings was also conducted. During the corrosion testing, the release of Ni-ion from uncoated and coated materials was confirmed. In addition, the Vickers microhardness and wear test were used to assess the coating's mechanical properties, and the results of these tests are shown below. The development of the HAP layer was confirmed by the XRD of the coated sample. An increase in the number of pulses significantly enhanced the microstructure and growth of the HAP film, as shown by SEM. However, Jafari *et al.* [11] used the electrophoretic deposition approach to coat synthetic HAP on 316L for varying amounts of time (between 1 and 5 minutes) while maintaining a constant potential of 60 V. Electrochemical studies were conducted on bare and HAP-coated SS316L in biomimetic conditions. HAP-coated samples display a more noble change in the corrosion potential and corrosion current density compared to uncoated samples regarding the corrosion properties derived using open circuit potential and potential dynamic polarization. Rakngarm *et al.* [12] created a bio-active coating by employing a layer of HAP on metal-made implants within the humanoid body to take advantage of the mechano-chemical characteristic of metal-made implants and the bio-medical compatibility of human body tissues for the HAP surface.

A literature survey indicates that compared to uncoated SS316L, the corrosion resistance of SS316L treated with a HAP layer is much higher [13]. Therefore, there is a need to study the mechano-chemical properties of the HAP powder-coated SS 316L to protect it against corrosion and biodegradation. In this context, a literature review is carried out to assess the mechano-chemical characteristics of SS316L, HAP, and HAP-coated SS316L.

Biomedical materials

Substrates

Among the many materials used in medicine, the stainless-steel type (SS 316L) is a popular choice for implants in orthopedic surgery because of its resistance to corrosion, strong mechanical capabilities, and low cost. Hip and knee replacement pins, screws, and other orthopedic implants are often made of stainless steel. However, scientific trials reveal that the corrosion from SS316L implants results in the release of metal ions from implants into the body tissues, which might have adverse effects. Also, the fact that corrosion failures have occurred while using devices made from these materials within the human body has paved the way for many studies to make these materials more biocompatible and corrosion-resistant. Mechanical properties of SS 316L and bone were tested on the tensile testing machine. Figures 1 and 2 illustrate the stress-strain diagram of SS316L and bone material, respectively. Table 1 compares the mechanical properties of SS316L to the natural bone. In this work, the elemental composition of SS 316L was assessed by Oxford Instruments-manufactured Foundry Master Spectrometer (Uedem, Germany). Table 2 shows an elemental analysis range for SS316L. The chemical composition for SS316L shows good agreement with the literature data [14-18].

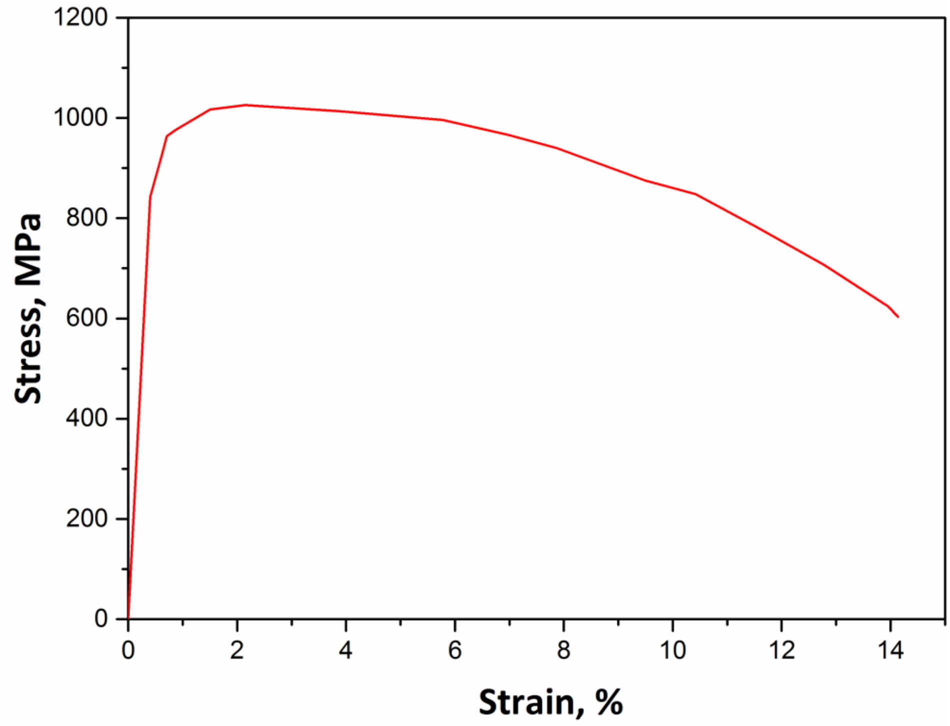

Figure 1. *Stress-strain diagram of SS 316L*

Table 1*. Various mechanical properties of bone and SS 316L*

No.	Properties	316L	BONE
1	Elastic modulus, GPa	210	10-30
2	Tensile stress, MPa	485	70-15
3	Tensile yield stress, MPa	170	120

Table 2. *Elemental composition for SS 316L*

Element	C	Mn	Si	Co	P	S	Cr	Mo	Ni	Fe
Content, wt.%	0.005	1.02	0.135	1.69	0.083	0.005	16.60	1.69	10.35	Balance

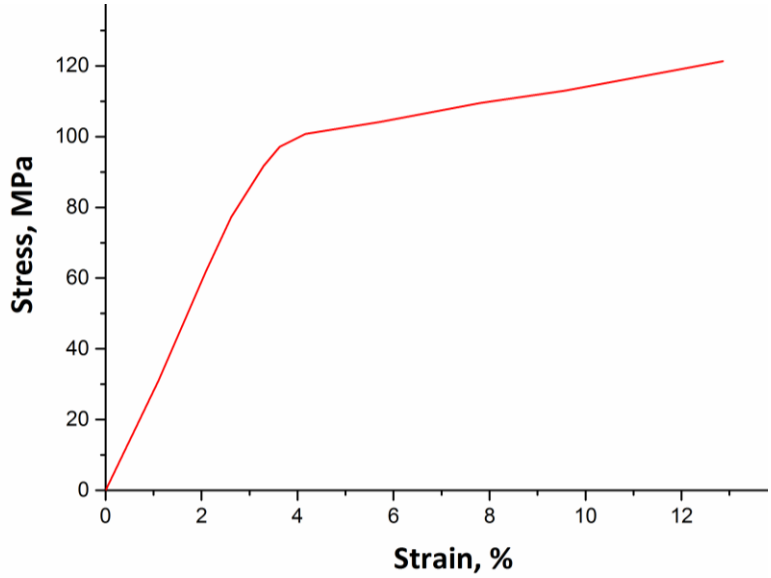

Figure 2. *Stress-strain diagram of bone material*

Hydroxyapatite: structure and properties

A ceramic material known for its medical applications is hydroxyapatite [19]. The bone material is composed of apatites which act as packing for Ca, Mg, P, and Na to strengthen the skeleton. Mineral HAP apatites ($Ca_{10}(PO_4)_6(OH)_2$) and brushite ($CaHPO_4\times2H_2O$) have structural similarities with biological apatites. There are two stable calcium phosphate phases in bodily fluid and temperature: the brushite phase at (pH<4.2) and the HAP phase at (pH>4.2). Crystals of hydroxyapatite have a hexagonal, rhombic prism shape. Hydroxyapatite has the lattice configuration (a = 0.9432 nm) and (c = 0.6881 nm), as given in Figure 3. Corners of the base plane are hotspots for producing hydroxyl ions (OH^-). Ions are arranged to be parallel to the c-axis of the crystals and transverse to the base plane of the crystals at every 0.344 nm (1/2 of the unit cell).

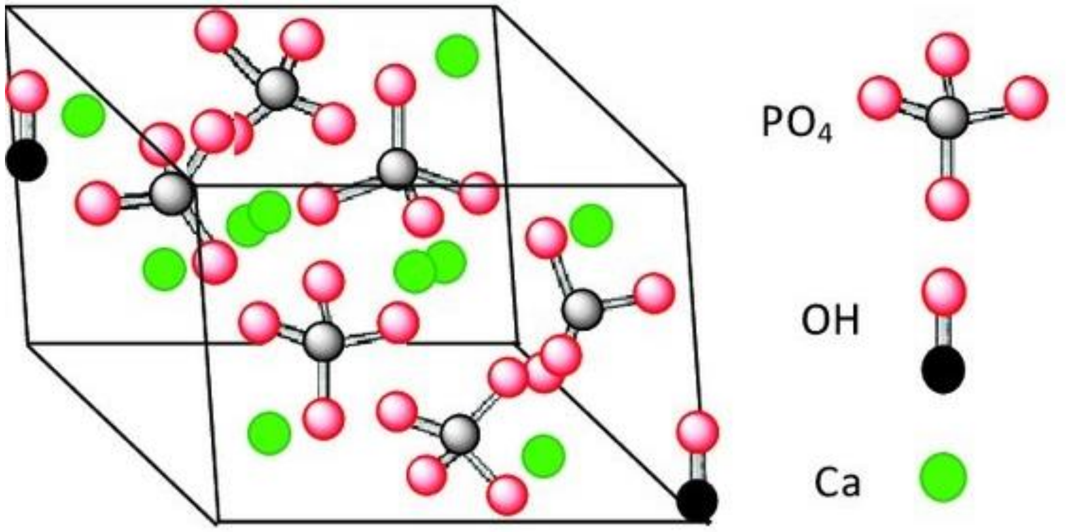

Figure 3. *Simplified crystal structure of hydroxyapatite* [21].
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Thus, about sixty percent of the Ca-ions in the crystal lattice are linked to the OH ions. HAP has a density of 3.219 g cm^{-3} [20]. HAP utilized in bones, hip replacement, and dental metal implants are generating around $2.3 billion in yearly sales, which is expected to rise. The success of implants is contingent on many aspects, including those related to biocompatibility and mechanical features.

Owing to corrosion concerns, the use of metals within the human body has been minimal. Morphologically, the HAP powder seems blocky and irregular in shape, as presented in Figure 4.

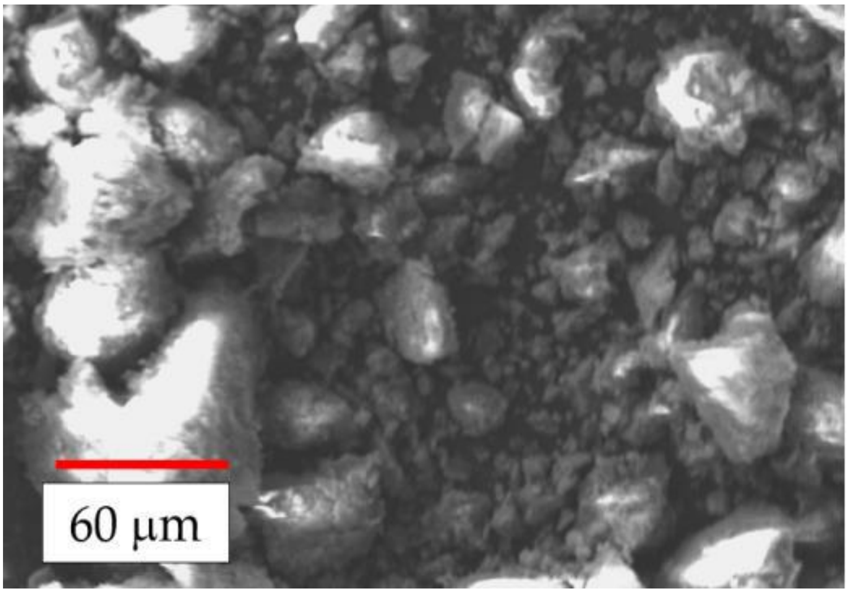

Figure 4. *SEM image of hydroxyapatite powder* [22]
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Coatings

Surface engineering plays a crucial role in protecting biomaterials used in implants. It protects against corrosion, biodegradation, and erosion [18,23-38]. Various coating processes are used to enhance the surface of engineering and biomedical materials [39-42]. Electroplating, electroless plating, hot dipping [43-49], vapor deposition techniques (physical [50-56], chemical [57-59] and electrochemical [60]), thermal spraying [61-63], claddings [64-75], plasma spraying [76-83], and electrophoretic deposition are all methods used to deposit coatings onto metals (EPD). As seen in Figure 4, the size of HAP powder depicts that larger as well as smaller particles were present. Moreover, the particle melting and layer formation phenomenon depends upon the coating technology as well as particle properties. Therefore, the HAP can be deposited to different materials in different thicknesses by following the different procedures, as illustrated in Figure 5. Figure 6(a) presents the SEM images of HAP coating on Ti6Al4V. Figure 6(b) presents the XRD of the HAP electrodeposited coating, which shows the presence of different crystals, namely stoichiometric HAP and -tricalcium phosphate (-TCP) in the as-coated surface.

Natural bone

In its mature form, bone is a biphasic composite. Collagen, a kind of protein, and HAP, a mineral phase that does not undergo chemical reactions, are its primary components. It is difficult to determine which phase is the primary load-bearer; maybe crystal serves as a filler to harden the collagen by limiting its mobility when stressed. Collagen is just 1 % as rigid as the mineral. Thus, it can't be relied upon to support bending or compressive forces. Only collagen contributes to the bone's fibrous structure. HAP is twice as powerful and significantly more rigid (Table 3).

Bone development involves inserting tiny platelets of HAP into predetermined pores in collagen, creating a composite of around two-thirds inorganic. Because of this, the fiber comparison only works if it is considered a composite itself, reinforced with platelets because the bone is not homogenous even at the morphological level [85].

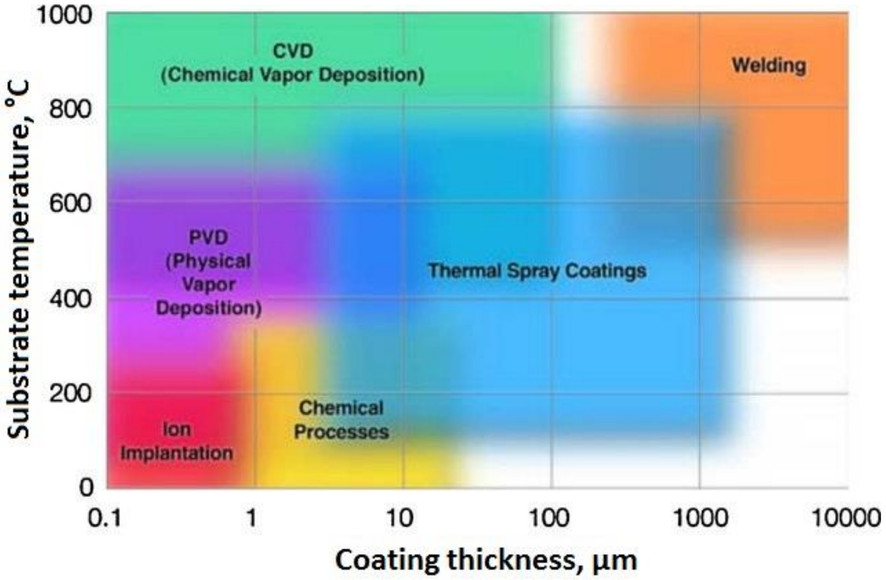

Figure 5. *Substrate temperature versus thickness of coatings deposited by different processes* [84] *(CC BY 4.0 Attribution)*

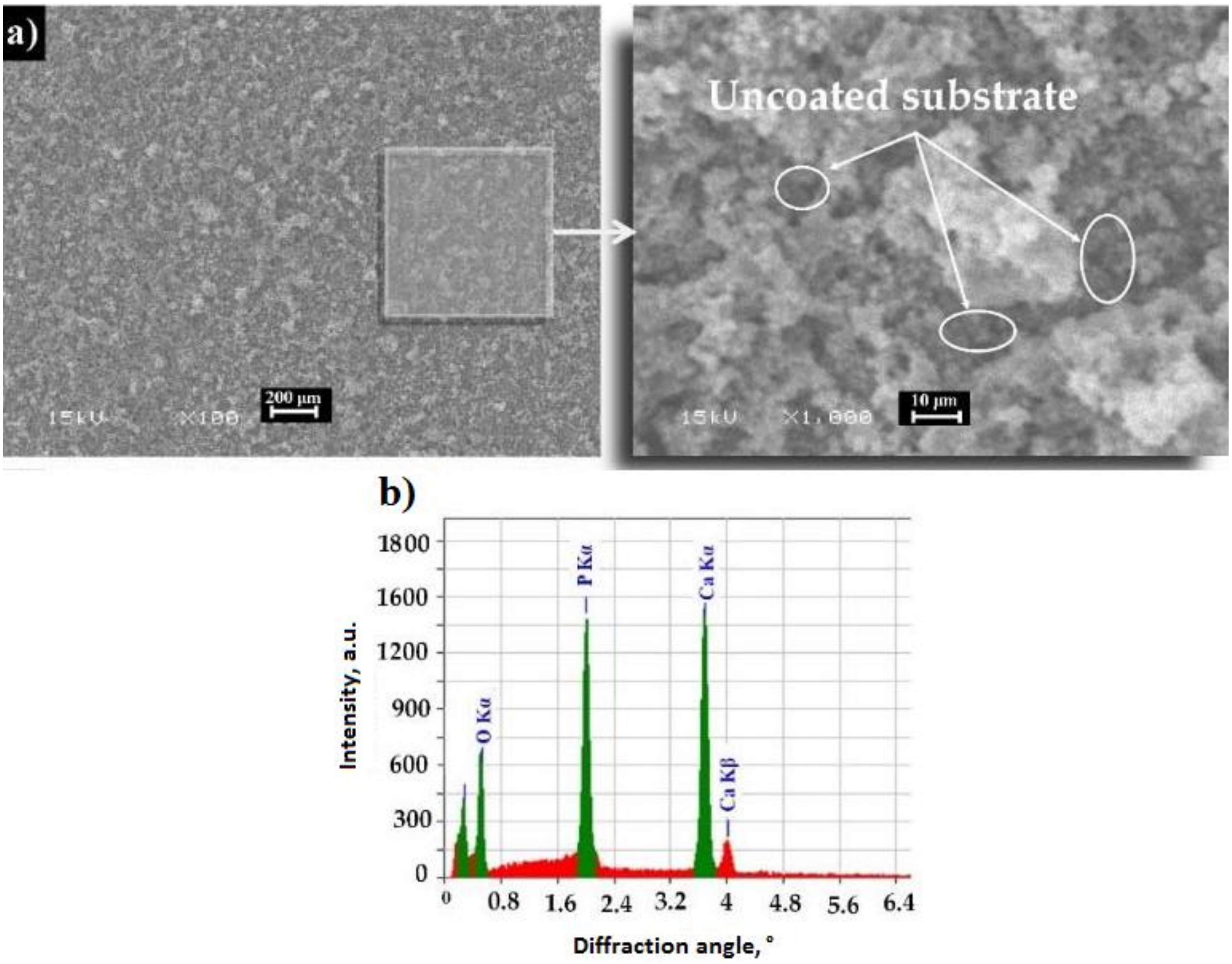

Figure 6. *(a) SEM and (b) XRD of hydroxyapatite* [22] *(CC BY 4.0 Attribution)*

***Table 3**. Material properties of the bone material [86]*

No.	Feature	Value
1	HAP ultimate strain	0.001
2	HAP strength, GPa	0.1
3	Collagen's strength, MPa	50
4	HAP stiffness, GPa	130
5	Stress acting on collagen for 0.001 strain, MPa	1

Figure 7 illustrates that bone has a complicated hierarchical structure that has an effect on its mechanical performance. The magnitude and direction of the stresses that bones can withstand and how these stresses are transmitted to the rest of the body are both controlled by the density and configuration of mineralized platelets. There are two primary ways in which collagen fibrils may be arranged: firstly, randomly (woven bone), and secondly, inlayers with desired orientation (lamellar bone). Primary lamellar bone consists of stacked layers of lamellae in a single plane, whereas secondary lamellar bone, Haversian bone, and woven bone all form cylindrical stacks of lamellae (laminar bone). In compact bone, you may find each kind [85]. An osteon is a fundamental unit of the skeletal structure. A hollow tube, approximately 200 m in diameter and 1-2 cm in length, serves as a weight-bearing component and a blood artery. Osteon walls are constructed using a coiled pattern of fine fibers (*i.e.* helical) of collagen interrupted by neighboring platelets of hydroxyapatite. As a consequence, compressive loads may be successfully carried by a small column, preventing buckling. However, its primary purpose is not durability [85].

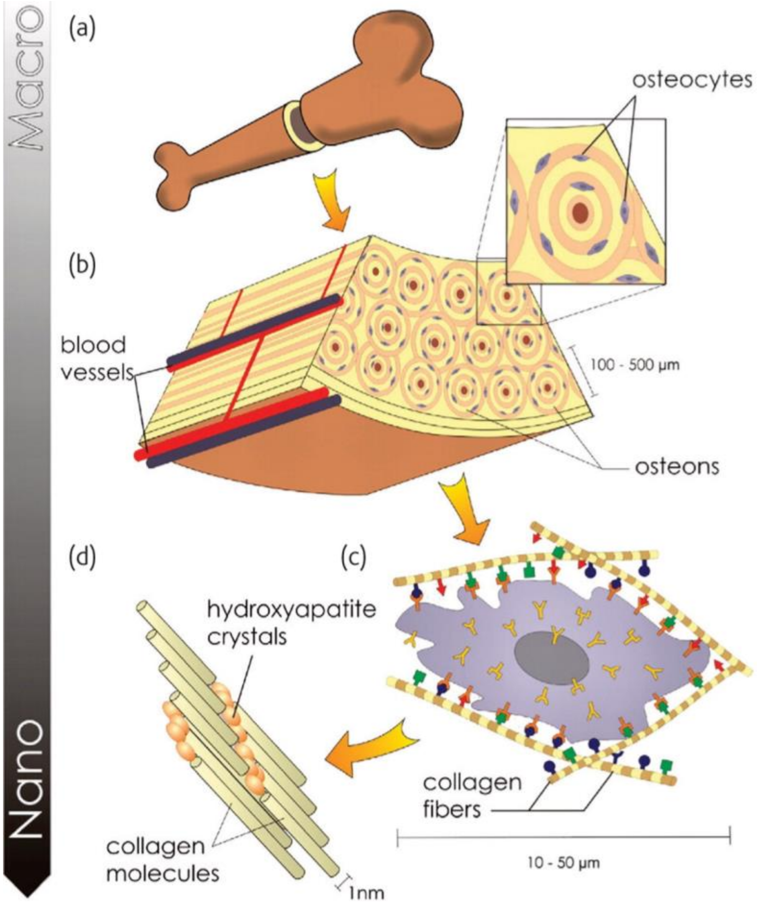

***Figure 7.** (a) Hierarchical structure of osseous tissue, (b) cylindrical Haversian systems or osteons, (c) cells are covered in a cluster of cell membrane receptors that react to particular binding sites, and (d) well-organized nano-structure of the surrounding extracellular matrix* [91]. *(CC BY 4.0 Attribution)*

Conventional orthopedic

Sir John Charnley's groundbreaking research is essential to the current generation of implant designs [87]. The metallic component (named femoral) may be made of SS316L metallic alloys, such as cobalt-chromium-molybdenum, cobalt-nickel-chromium-molybdenum, or titanium-aluminum-vanadium alloys, while the UHMW (ultra-high molecular weight polyethylene) covering the femoral head may be manufactured of synthetic materials (Figure 8). PMMA bone cement is used to secure the devices in place. The current methods are temporary. As a result, 10 to 20 % of implants need replacement after 10 years, and some may require replacement even sooner, within the first 5 years [88]. Such short lifespans may be attributed to loosening, erosion-corrosion, the action of uneven loading, and irritation in the body tissues. Charnley [89] suggested that such types of implants can be used only for aged patients due to short life expectancy because of the very short lifetime for these implants owing to inadequate cement technology. A second characteristic that might interfere with implant function is stress shielding. Load misallocation at the bone-implant contact is a cause of implant dislocation or loosening [90]. This issue is present in all currently used metal implant components.

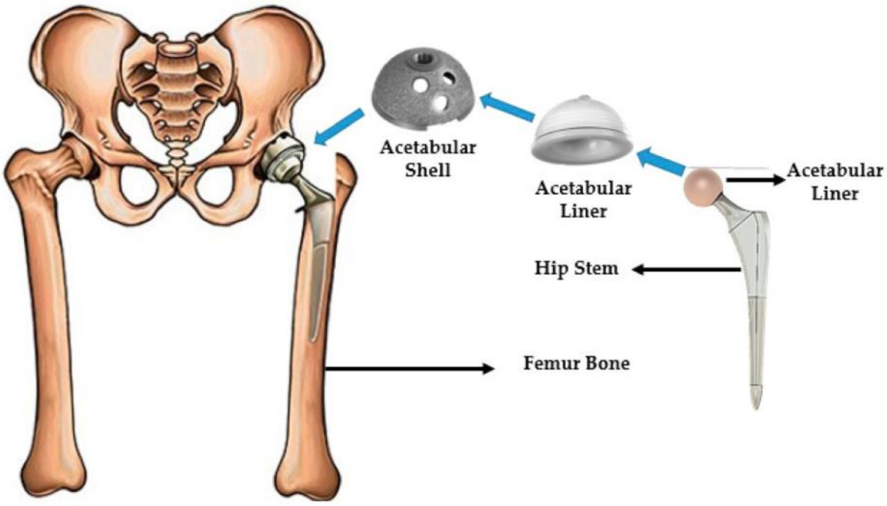

Figure 8. *Model of an implanted total hip prosthesis* [92]. *(CC BY 4.0 Attribution)*

Conclusion and future prospective

In conclusion, metals may be used in a wide variety of contexts. And one of these sectors is medicine, which benefits from traits like strong strength, among many others. However, there is another side to metals: they tend to corrode when used in harsh environments like the one found within the human body. Although HAP has long been used to promote bone regeneration by conduction or as a scaffold for filling defects, recent advances in our understanding of its osteo-inductive characteristic indicate that it may soon play an even more important role in fostering new bone growth. Previously unimaginable clinical applications for HAP coatings are now a reality because of advances in technology. As a key component in the formation of calcified tissues, nanostructured calcium apatite is crucial. The nanostructured material may mimic the fundamental structure of bone and other calcification tissues by attaching biological molecules like proteins, and it can also synthesize controlled structures of apatite. Novel nanostructured biomimetic and biocompatible materials are needed for the regeneration process. Composites containing nanostructured bio-ceramic particles have the potential to increase the durability of injectable and controlled-setting synthetic bone implants and bone cements. The potential of nanotechnology for bone regeneration is the subject of intensive study in the future. Additionally, nanostructured coatings have shown great promise in many other industrial applications. Therefore, HAP-based nanostructured coatings can be a topic of interest among researchers in the future. The coating is only one method that may protect these metals against corrosion or reduce their effects to an acceptable level. Additionally, as time went on, improvements were made to the coating process, and new coating materials were tested to find the healthiest and safest for human use. Several studies have shown that the combination of HAP with other metals increases the body's natural resistance to corrosion. Moreover, the HAP coating on Ti6Al4V has shown the uncoated surface sites with the electrodeposition process. Therefore, a suitable technique is required to be followed for future work.

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