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Review paper

Bioactivity and corrosion analysis of thermally sprayed hydroxyapatite based coatings

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Abstract
Metallic biomaterials have been used to repair and replace human body parts because of their excellent biocompatibility, strong corrosion resistance, and high mechanical properties. A ceramic biomaterial that is highly suitable for coating on metallic biomaterials is hydroxyapatite. This is because it is biocompatible with synthetic and natural bone tissue. There has been a growing interest in HAp-based coatings using thermal spray techniques to enhance the crystallinity and adhesion quality and produce a dense coating of metallic biomaterials. Thermally sprayed coating material has been studied and reviewed in detail in the bioactivity analysis and electro-corrosion analysis. Furthermore, the bioactivity of HAp coatings is determined by their ability to promote bone formation and osseointegration and a valuable understanding of the mechanisms and current advancements in bioactivity. Additionally, the corrosion behaviour of thermally sprayed HAp coatings under simulated conditions has been reviewed.

Keywords
Biocompatibility; biomaterials; surface engineering; plasma spray; bio-implants; fixation devices

Introduction

Every year, approximately 2.2 million patients worldwide receive bone grafting procedures because of bone-related diseases that cause fractures [1]. Additionally, the population of the planet is growing yearly. Therefore, it is not an exaggeration to state that the need for implants to address bone issues is growing daily. Worldwide, arthritic joint replacement, osteoporosis, hip and knee replacements, correction of spinal fractures, long bone fracture fixation, and other orthopaedic and maxillofacial reconstruction applications are among the many implants uses. Improved implants with superior biocompatibility and high functionality are in great demand because of the previously indicated increase in implant demand [2].

To improve a patient's quality of life, metallic biomaterials are vital for failed tissue, particularly failed hard tissue, bone repair, and fracture fixing. This is a result of their extreme durability, toughness, and strength. However, a concern with orthopaedic implants is their deficiency of biocompatibility. The disadvantages of implants include high corrosion rates, a lack of anti-infection properties, and implant loosening because of wear debris particulates, which are toxic to human health. Therefore, in implants, one of the main issues is premature failure. For orthopaedic implants to survive over the long term, it is crucial to enhance their qualities by reducing the drawbacks. Applying a bioactive material coating to implants is one way to enhance their characteristics and lifespan [3].

Hydroxyapatite [HAp, $Ca10(PO_4)_6(OH)_2$] coating is by far the best of the several bioactive materials that are used to make implants, and it has been applied clinically to many orthopaedic sectors. Owing to its osteogenic qualities and capacity to establish robust connections with the host bone tissues, HAp has been used in calcium phosphate bioceramics to cover metal prosthetics. To create the HAp coating, numerous techniques are available. The choice of coating method and associated process parameters can affect the HAp coating's mechanical characteristics, phase composition, and crystallinity [4]. By adding HAp coatings to metallic substrates, inert metallic materials become bioactive and aid in osseointegration the process by which implants directly fuse with surrounding bone tissue, enhancing implant durability and long-term performance.

Hydroxyapatite (HAp) is often deposited on the surface of substrate implants to enhance their bioactivity in the bone by forming a factual joining with the bone tissue. Implant osseointegration development needs to be improved so that the device can fuse with the surrounding bone tissue properly. That is precisely what this approach does. After a while, the hydroxyapatite coating improves soft tissue adaption, looks better, and forms a hydroxyapatite layer necessary for bone growth and finally strengthens the bond between the implant and bone tissue [5].

HAp-based thermally sprayed coatings have attracted significant attention because of their bioactive properties and resilience to corrosion. Because of their bioactivity, these coatings have been demonstrated to help injured tissues, reduce bacterial adhesion, and enhance corrosion resistance, making them ideal for a range of biomedical. HAp coatings have been demonstrated in numerous studies to interact chemically and physiologically with body fluids while possessing antibacterial properties.

Furthermore, by reducing the surface roughness value, these coatings lessen the adherence of germs [6-7]. The techniques for preventing corrosion are shown in Figure 1.

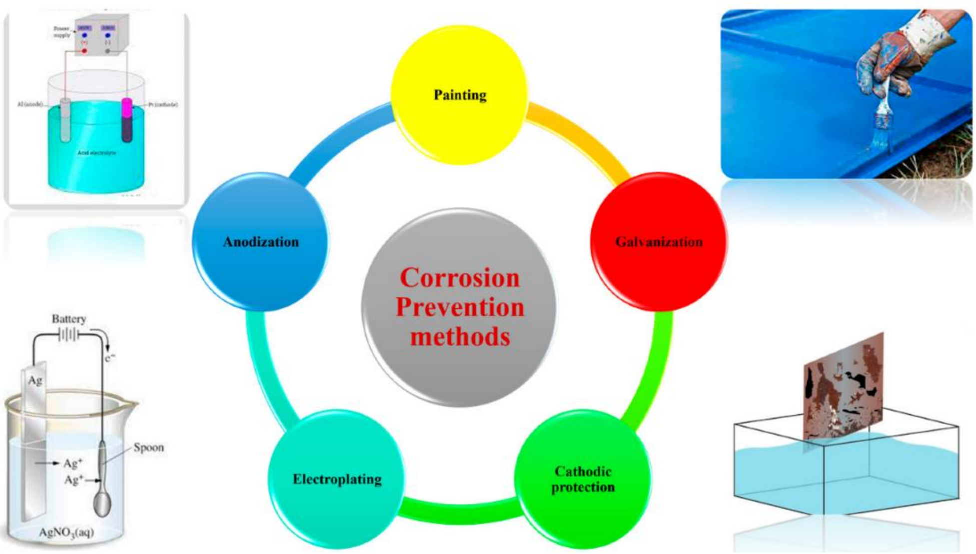

Figure 1. *Techniques for preventing corrosion [8] (CC BY 4.0 Attribution)*

Hydroxyapatite

The inanimate phase of bone areas contains HAp carbonate apatite, deficient in calcium. The phases HAp of calcium phosphate are utilized in bone replacement and repair of bone graft materials and as coatings on metallic implants to help fixation to the bone without cement because of their chemical resemblance to bone minerals [9].

HAp can be applied to metallic implants using a variety of coating methods. Metals' non-bioactivity aspect can be readily made up for by using HAp because the strong interaction between the coating and the implant with HAp coating promotes the growth of new bone. Moreover, HAp coating functions as a protective film against corrosive bodily fluids. Additionally, by delaying the pace at which metallic ions dissolve, this HAp coating reduces the likelihood of leaching, as well as increases their biological activity, and slows down the rate of disintegration. Furthermore, the coating containing HAp has better bone conductivity and biological activity [10].

There are numerous coating techniques available for applying HAp to metallic implants. High-velocity oxyfuel spraying (HVOF), dip coating, sol-gel, and flame spraying are some of these methods. Because thermal spray coating leaves a homogeneous layer on metal surfaces, it is currently the most effective and widely used method for coating metallic implants. Figure 2 shows the hexagon-shaped crystalline structure of HAp [11].

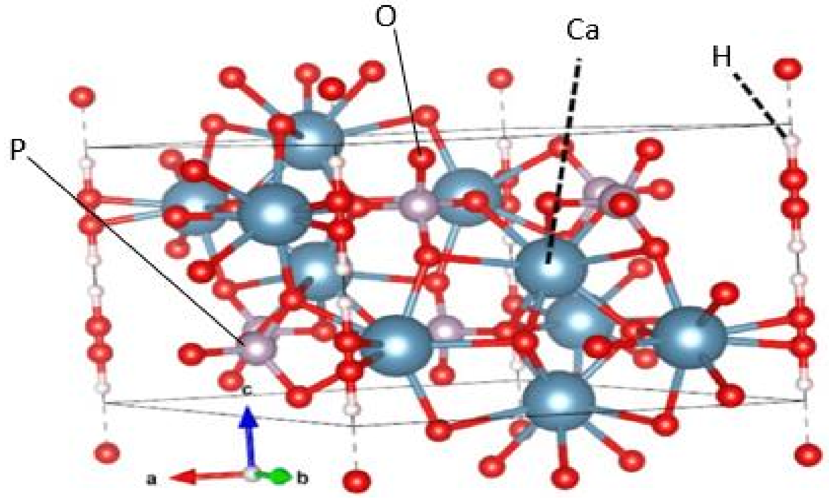

Figure 2. *Hexagonal crystal structure of HAp [12] (CC BY 4.0 Attribution)*

Antibacterial efficacy

The ability of a substance or material to effectively suppress or eliminate germs is referred to as antibacterial effectiveness. The antibacterial qualities of hydroxyapatite, a biocompatible substance that is frequently utilised in dentistry and medicinal applications, have drawn interest.

Research indicates that the antibacterial activity of HAp can be markedly increased by doping it with components. It has been discovered that some elements, including cerium, magnesium, zinc, and silver, significantly improve HAp's antibacterial capabilities. Several previous investigations have shown the strong antibacterial activity of doped HAp against a range of human pathogenic microorganisms. For instance, Ag/Mg and Ag/Zn doped HAp showed strong antibacterial activity.

Using techniques like microwave-assisted combustion, it has been possible to synthesise HAp with antibacterial qualities, demonstrating its promising potential. Moreover, dopant compounds can modify HAp, which does not naturally possess antibacterial capabilities and can demonstrate antibacterial activity. The creation of sophisticated antibacterial materials with HAp is made possible by these discoveries [13,14].

Adhesive strength

The main issue that arises when coating HAp on a metallic surface is inadequate HAp binding. This results from the low adhesive bond between the HAp layer and metallic load-bearing locations. Because of HAp's poor crystalline structure, HAp film connection on the metallic surface begins to decrease and eventually fails.

As the metal surface begins to expose itself to the body's environment, this failure causes the release of metallic ions. Surface modifying chemicals help produce a strong layer over the metallic surface and are necessary to improve the adherence of HAp films [15]. Figure 3 illustrates the bonding mechanism of thermal sprayed coating.

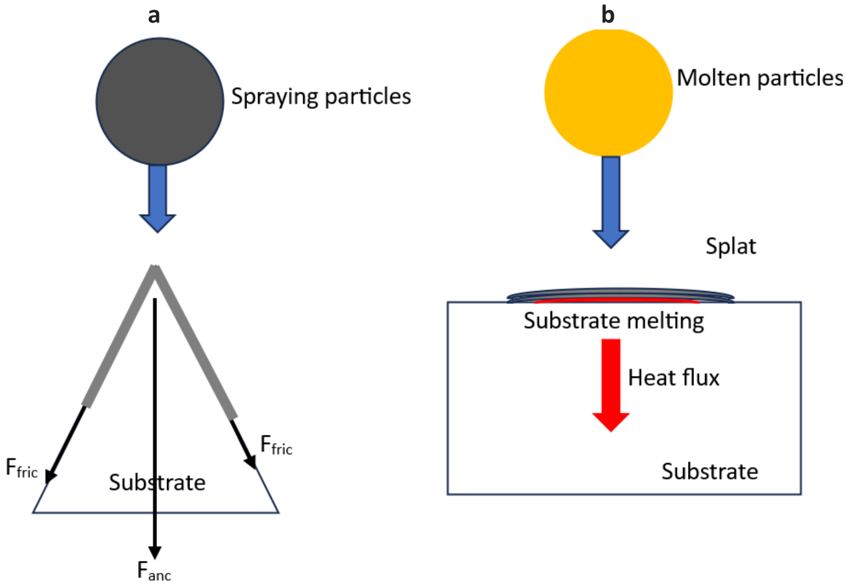

Figure 3. *Thermally sprayed coating mechanism: (a) mechanical anchor, (b) metallurgical bonding [16] (CC BY 4.0 Attribution)*

Adhesion and cohesion

An attractive force holding the two surfaces together is called adhesion between different layers. To keep the two surfaces apart, this force opposes the imposed stress. Adhesives are non-metallic substances applied to two surfaces to prevent their separation by binding them together. Applying adhesive has several benefits, such as stress distributions, processing simplicity, aesthetic appeal, and reduced processing costs. This glue connects the two surfaces with a significant binding force by penetrating the substrate's microchannels. Numerous additional forces operate on the layers when adhesives bind disparate surfaces. These forces consist of chemical forces, mechanical interlocking, and physical adsorption.

The substrate and adhesive form hydrogen bonds, which cause the adhesive layer to adhere to the substrate's surface. There is a chemical bond between the substrate and the coated substance. These chemical connections have a very high strength, which helps the coating resist deterioration from the outside environment.

For improved adhesion between the adhesive and substrate, the rough surface increases the interfacial area. To fully wet the surface, adhesive needs to have wetting capabilities to provide the best outcomes. It dries out and becomes stronger after application, sharing and transmitting the load amongst the neighboring layers [17].

The intrinsic force of attraction between molecules in a coated film is known as cohesiveness. It is essential to guarantee the coating's efficacy and longevity. Because it keeps the coating from flaking off or delaminating over time, especially in harsh environments or when the coated surface is subjected to mechanical stress, high cohesiveness is very significant. It takes a variety of criteria, including coating material formulation, surface preparation, and application technique, to successfully establish high cohesion in HAp coatings.

The cohesiveness of the coating is essential to guaranteeing the long-term efficacy and stability of the medical implants since HAp coatings aim to stimulate bone formation and facilitate implant integration [18].

Metallic biomaterials

Biomaterials that closely resemble the original material they intend to replace are frequently the most successful. High strength, Young's modulus compatible with bone-to-load wearing, porosity, low density and resistance to corrosion and wear are necessary for biomaterials intended for use in orthopaedics and load-bearing applications [19].

Metallic biomaterials are widely used in orthopaedic implants, dental implants, and cardiovascular devices. They are mostly composed of metals like titanium, stainless steel, and cobalt-chromium alloys [20]. The various metal implants used in the human body are shown in Figure 4.

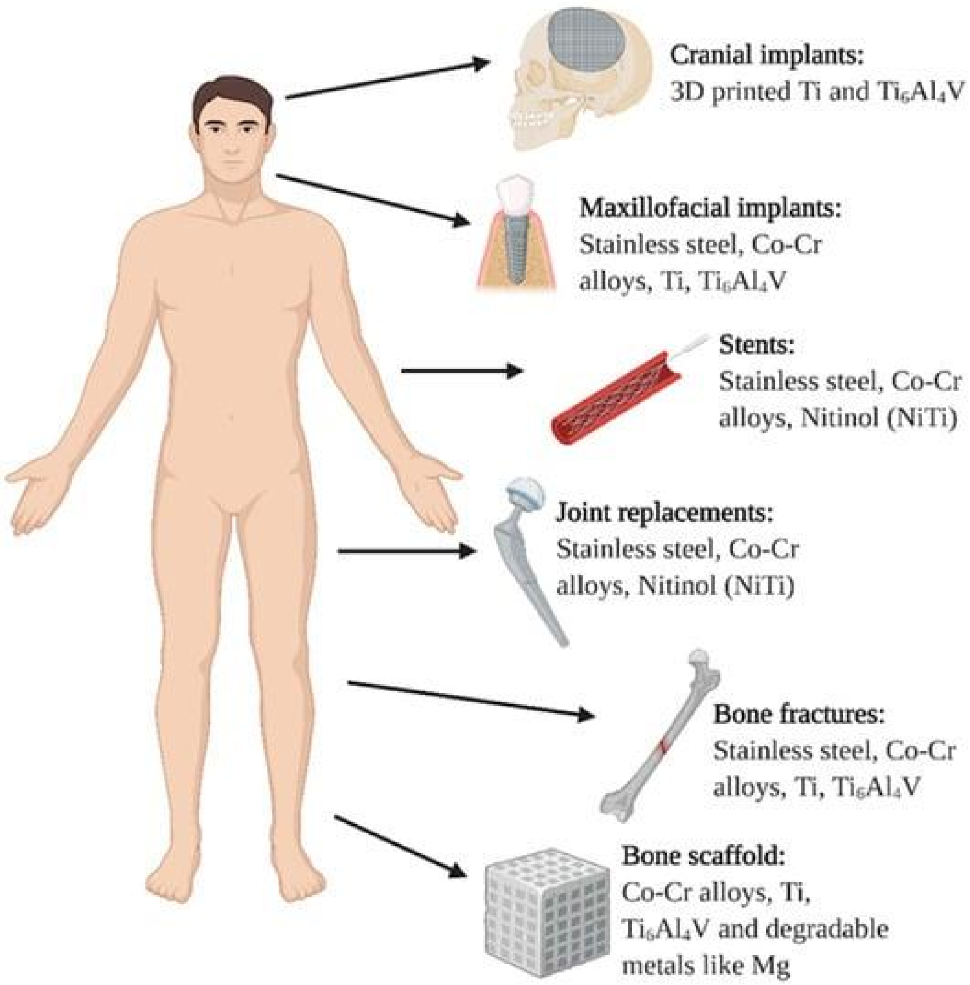

Figure 4. *Metal implants used in the human body [21] (CC BY 4.0 Attribution)*

Bone engineering, a method to regenerate injured bone tissue, focuses on creating a bionic system that combines cells, scaffolds, and bioactive substances to enable repair [22]. The n-HAp composite scaffolds with added bioactive substances and therapeutics exhibit a high capacity to promote the growth and repair of bone tissues. Usually utilized bioactive chemicals are lipids, flavonoids, hormones, peptides, amino acids, and protein growth factors. Furthermore, drugs including alendronate, deferoxamine, dexamethasone, simvastatin, and antibiotics like ciprofloxacin, moxifloxacin, and gentamicin have been used to promote bone regrowth and prevent infections [23].

Bioactive agents for bone defects are placed into an n-HAp composite scaffold as shown in Figure 5.

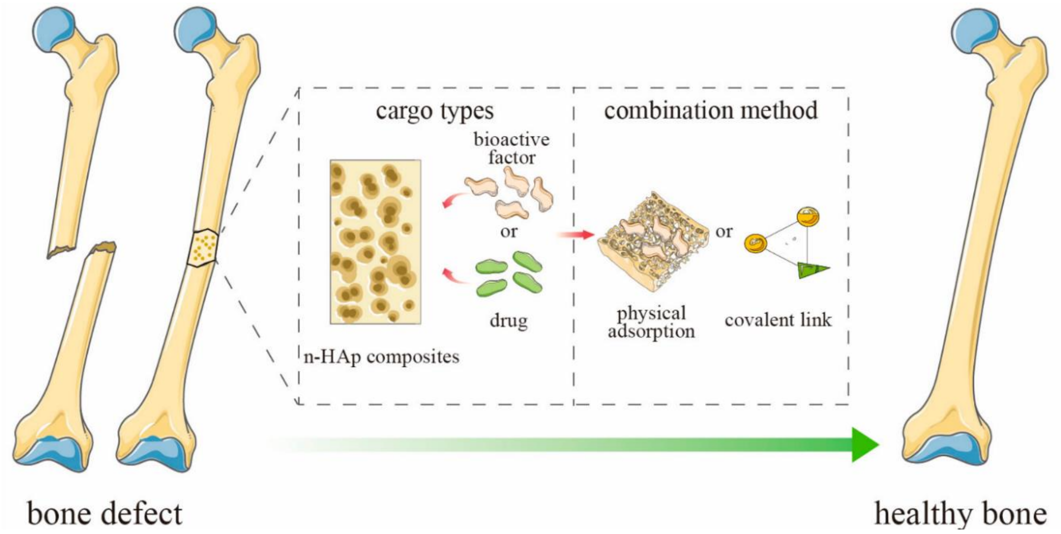

***Figure 5.** n-HAp composite scaffold for a bone deficiency filled with bioactive substances or medications [27] (CC BY 4.0 Attribution)*

Deposition by thermal spraying

Thermal spraying is useful for biomedical applications, including orthopedic and dental implants, for applying HAp coatings on substrates. There are certain unique issues and difficulties with the adherence, crystallinity, and biocompatibility of the coatings when HAp is deposited using thermal spraying techniques [24].

Flame spraying

The flame spray coating for biomedical implants has various advantages. It generates coatings that are resilient to corrosion, less poisonous, and capable of establishing a bond between bone and implants. This cost-effective process improves the wear-resistant, biocompatibility of implants and protects them from electromagnetic and radiofrequency interference. It will also enhance adhesion strength, microstructure, thickness modification, and phase structure control [25].

However, flame spray coating has several drawbacks, especially when applied to biomedical implants. Because of the extreme heat, strong UV light, and vapors containing potentially hazardous ingredients, there are dangers to one's health and safety throughout this operation [26]. Figure 5 shows the n-HAp composite scaffold for a bone deficiency filled with bioactive substances or medications.

Plasma spraying

Orthopaedics have made extensive use of metallic implants coated with plasma-sprayed HAp. The fundamentals behind plasma spraying are the use of electrical discharge between electrodes to create a plasma flame, which is then used to heat HAp particles to extremely high temperatures.

It is commonly known that throughout this thermal process, once the coating cools, there is partial apatite disintegration and the creation of numerous secondary phases, all of which can be succinctly summed up by the thermal stability of apatite. The plasma spray coating to biomedical metallic implants has been the subject of numerous studies [28].

The HAp and β-TCP coating on Ti using plasma spraying for orthopaedic and dental applications. It was discovered that a tuneable solubility of the composite coatings could be achieved for orthopaedic applications by choosing a particular composition and applying various heat treatments [29].

The correlation between the spray constraint, the frequency of dissolution, and the surface properties of coatings was found, and as the plasma power and spraying distance increased, the HAp's phase purity and crystallinity gradually declined. They demonstrated that significantly better particle melting occurred on coated surfaces sprayed at higher power and greater distances. It has also been observed that coatings sprayed at a greater power exhibited a pattern resembling bone apatite, while coatings sprayed at a lesser power had a crystalline HAp structure. The thick, adherent, and bioactive coatings can be produced using plasma spraying techniques, according to numerous studies [30].

Vacuum plasma spraying

One innovative technique used to apply highly functional coatings on biomedical implants is vacuum plasma spraying (VPS). Other advantages of the VPS techniques for deposition in biomedical implants are that the coating deposition is very rapid, coatings may be vacillatingly thin or thick, and the slow solidification of the coating allows the residual stresses to be contained. Lastly, it helps in new bone formation around the implant, which is critical to improving long-term efficiency. Biomedical implants thus benefit from VPS in terms of osseointegration, hardness, antimicrobial properties, coefficient of friction, wear resistance, and other mechanical and biofunctional properties of vacuum plasma sintering coatings [31].

High-velocity oxy-fuel (HVOF) spraying

HVOF spraying is an effective technique for coating deposition on biomedical implants. This intricate procedure produces thick coatings that are very wear-resistant, have a low porosity, and a strong binding strength [32].

Since the improvement in deposition efficiency and the consistency of the coatings made, the second method is now the most often mentioned way to alter the surface of biocompatible materials that come into touch with live tissue. The FDA has authorized atmospheric plasma spray (APS) as a thermal spray technique for the fabrication of bioactive coatings for medical devices. Several studies have used HVOF to limit the pace of HAp degradation by fabricating coatings. A HAp-based coating's corrosion resistance and bioactive behavior were both enhanced by this method [33].

Detonation spraying (or detonation gun)

The high-velocity thermal spray technique is widely used to provide medical implants with protective coatings, enhancing the devices' mechanical and biological properties. The ability to create coatings using detonation gun spray methods results from HAp's aptitude for easy deformation at elevated temperatures [34].

HAp-oriented crystals: a comparable droplet deposition technique reveals the same features. It is crucial to differentiate between the two phases inside the coatings because an amorphous phase might be produced by quickly cooling melts with a composition like HAp. Applying cathodoluminescence microscopy to the coated surface allows for the differentiation of crystalline zones [35]

Cold spraying

As a thermal spray technique, cold spraying involves forcing a compressed gas to expand at supersonic speeds through a converging-diverging nozzle. This extension enables the rapid production of coatings using powdered ingredients. High-pressure inert gas nitrogen is used in cold spraying (HPCGS), whereas compressed air is used in low-pressure cold spraying (LPCGS). Powder fusion does not occur when solid-state bonding is used to cling the sprayed powder particles to the substrate surface [36].

Therefore, when the deformation rates are 10^8 s^{-1} or higher, the particles' impact kinetic energy in the interfacial region between the substrate and the surface leads to the formation of viscoelastic or, with increasing speed, elastoplastic energy. In the future, the production of cold spray coatings arwill be based on the compaction of the material, causing the particles to stack due to solid-state impacts; thus, the characteristics of the form-dense coatings will be formed. It is possible to create cold spray coatings only because the sprayed powder has a certain ductility. Solid-phase powders of ceramic materials, particularly hydroxyapatite, have a brittle mechanical behaviour in the solid state and fall apart if it exceeds the elastic limit. So, the model and physical-mathematical predictions are not always true, and the established critical velocity in cold spraying for metals and other materials cannot be used to create coatings on ceramics [37].

However, Khlifi *et al.* [38] have specifically conducted a study on the hydroxyapatite of the HAp coatings' nanomechanical properties, adhesion, and corrosion resistance. Indeed, the HAp coatings on the Ti6Al4V alloy were deposited with the use of the electrodeposition technique. It was prepared at various concentrations of H_2O_2, which influenced the electrolyte and, shortly afterward, after the heat treatment. Furthermore, the surface of HAp coatings' morphologies before and after treatment and the subsequent cross-sections were analyzed with the help of scanning electron microscopy coupled with X-ray microanalysis for the identification of the phase and evaluate the composition via X-ray diffractometer. At the same time, corrosion resistance via electrochemical testing evaluated the uncoated, as-deposited, and heat-treated coatings with three concentrations of hydrogen peroxide 0, 6, and 9 % was conducted as well. Figures 6 and 7 illustrate the SEM-EDXS and XRD study results.

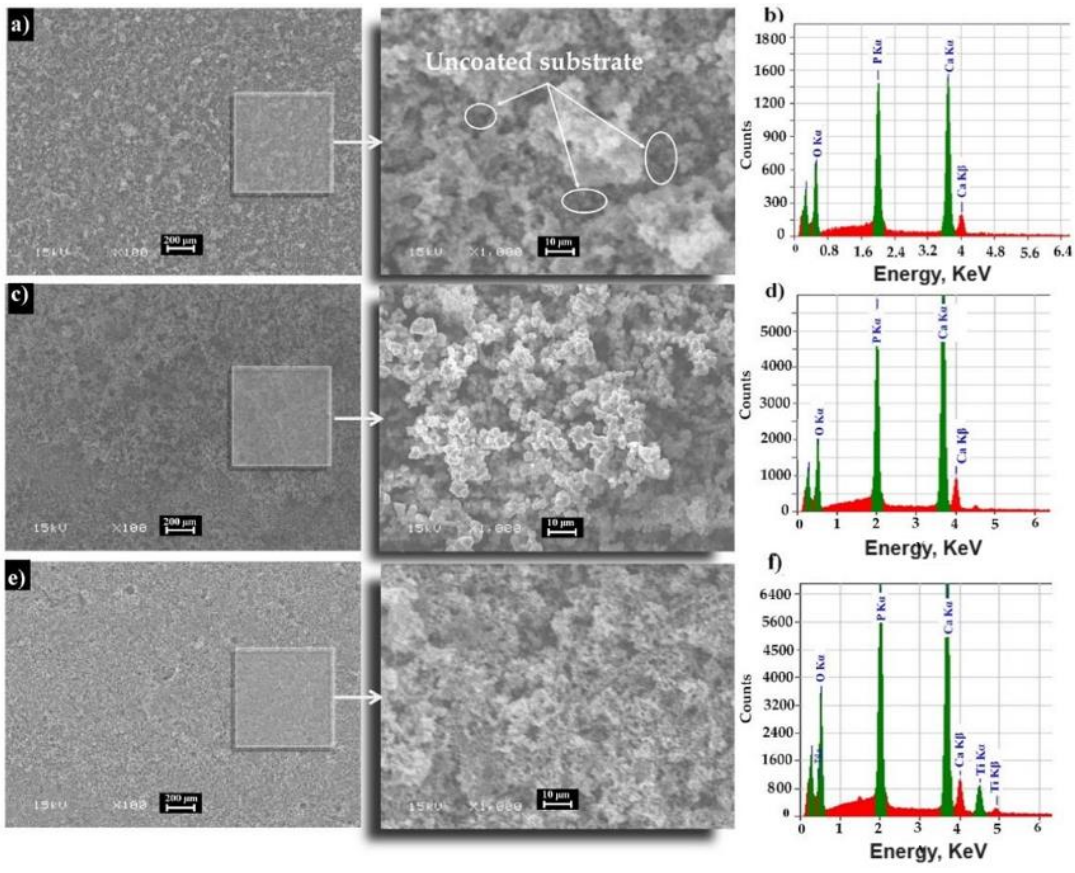

Figure 6. *HAp coatings with varying H_2O_2 contents were analyzed by SEM-EDXS: (a,b) 0 %, (c,d) 6 %, and (e,f) 9 %. for corrosion resistance of coatings [38](CC BY 4.0 Attribution)*

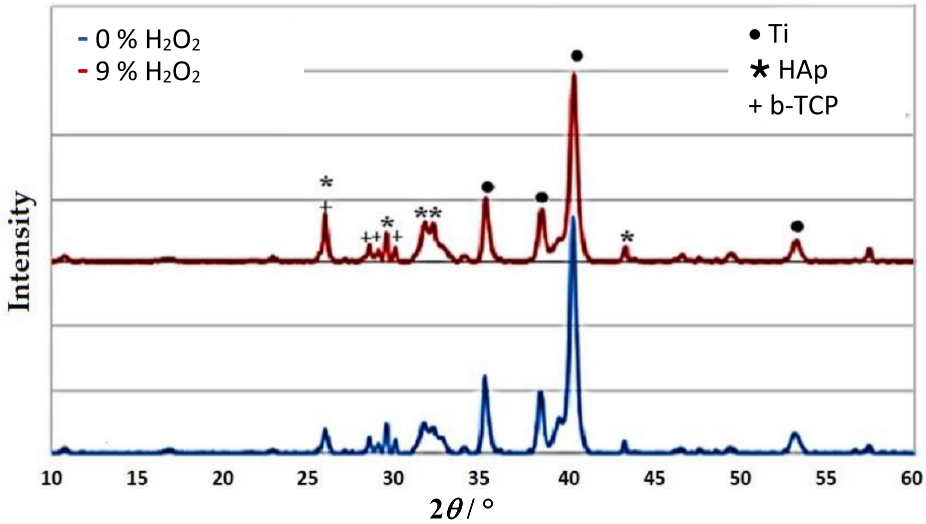

Figure 7. *X-ray diffraction patterns of HAp coating applied with 0 % and 9 % H_2O_2[38] (CC BY 4.0 Attribution)*

Bioactivity analysis

The most recent generation of functionalized bioactive bone substitute materials encourages the growth of new bone, catalyzes the body's regenerative process because of their exceptional mechanical strength, replaces the skeleton's supporting role, and allows for full regeneration of the original tissue because they are resorbable. However, the interaction of components to produce measurable biological reactions is the aim of the bioactivity analysis. It includes many things, such as how biological effects are measured, what influences bioactivity, and possible uses. Bioactivity is measured using a variety of techniques, including as functional metabolomics, *in vivo* and *in vitro* procedures, and methods in simulated body fluids (SBF) to test their biocompatibility. The potential for apatite production on the surfaces can be examined in these model fluids. The only constituents of most SBFs present in the same concentration as the natural fluids are the inorganic ions of blood plasma; no proteins, amino acids, or vitamins are present. There are two possible types of tests: dynamic and static. Given the continuous movement of body fluids, the dynamic approach may be a more accurate means of assessing biocompatibility. Static tests, on the other hand, are more commonly used and less complex in the literature. However, the outcomes of these tests do not always align with the findings of the *in vivo* tests, indicating that the *in vitro* trials are insufficient to accurately assess the bioactivity of the artificial materials [39]. Biocompatibility can also be determined by using stem cells. Cell investigations can produce more accurate evidence of bioactivity than SBF tests, but they are far more expensive and need sterile laboratory conditions and suitable microscope equipment [40]. Table 1 shows the bioactivity analysis of various materials coated with HAp.

Blum *et al.* [41] have used the simulated bodily fluid (SBF) solution in the *in vitro* bioactivity test. The HAp-coated Ti rod was immersed in the 100 mL SBF solution for 28 days, whose pH value was adjusted to 7.4, and during the test, the temperature was maintained at 37 °C. After the test, the coated rod was dried at 100 °C for 1 day and was examined using an SEM and XRD.

Patty *et.al.* [43] examined the titanium coating's mechanical properties and bioactivity using hydroxyapatite and bovine collagen. Based on the supposition that the surface apatite's nucleation capacity is connected to its bioactivity, the SBF test is the sole chemical model offered as a gauge of the implant surface's biological activity.

Figure 9 shows the SEM images of Ti/HAp-1, Ti/HAp-3, and Ti/HAp-coll before SBF immersion. Ti/HAp-3's solid-agglomerate surface results from the high HAp content (3 %), although Ti/HAp-1 and Ti/HAp-coll exhibit porous surfaces following calcination. During the ten days of SBF immersion, every sample exhibited a compact HAp block and a fully enclosed surface shape. On Ti/HAp-1 and Ti/HAp-3, the HAp block diameter was 1-2 µm, but on Ti/Hap-coll, it was 3 to 5 µm.

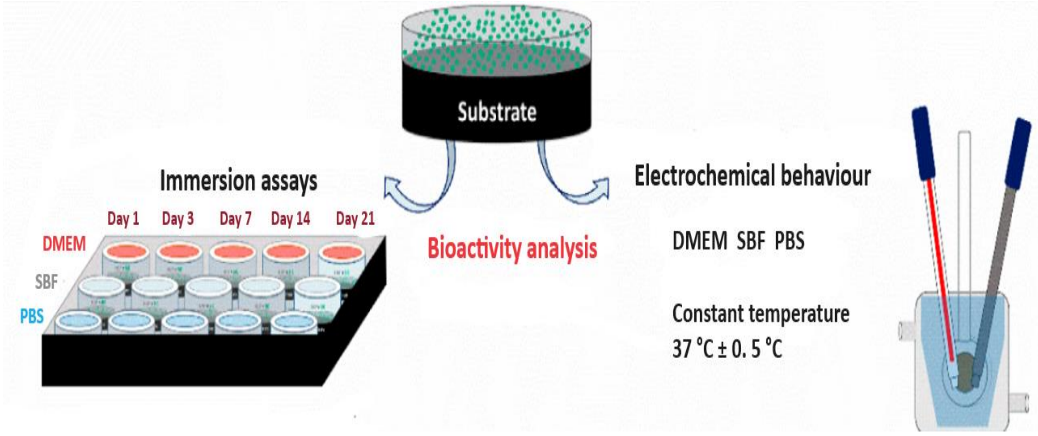

Figure 8. *Schematic illustration of the experimental setup of bioactivity analysis [42] (CC BY 4.0 Attribution)*

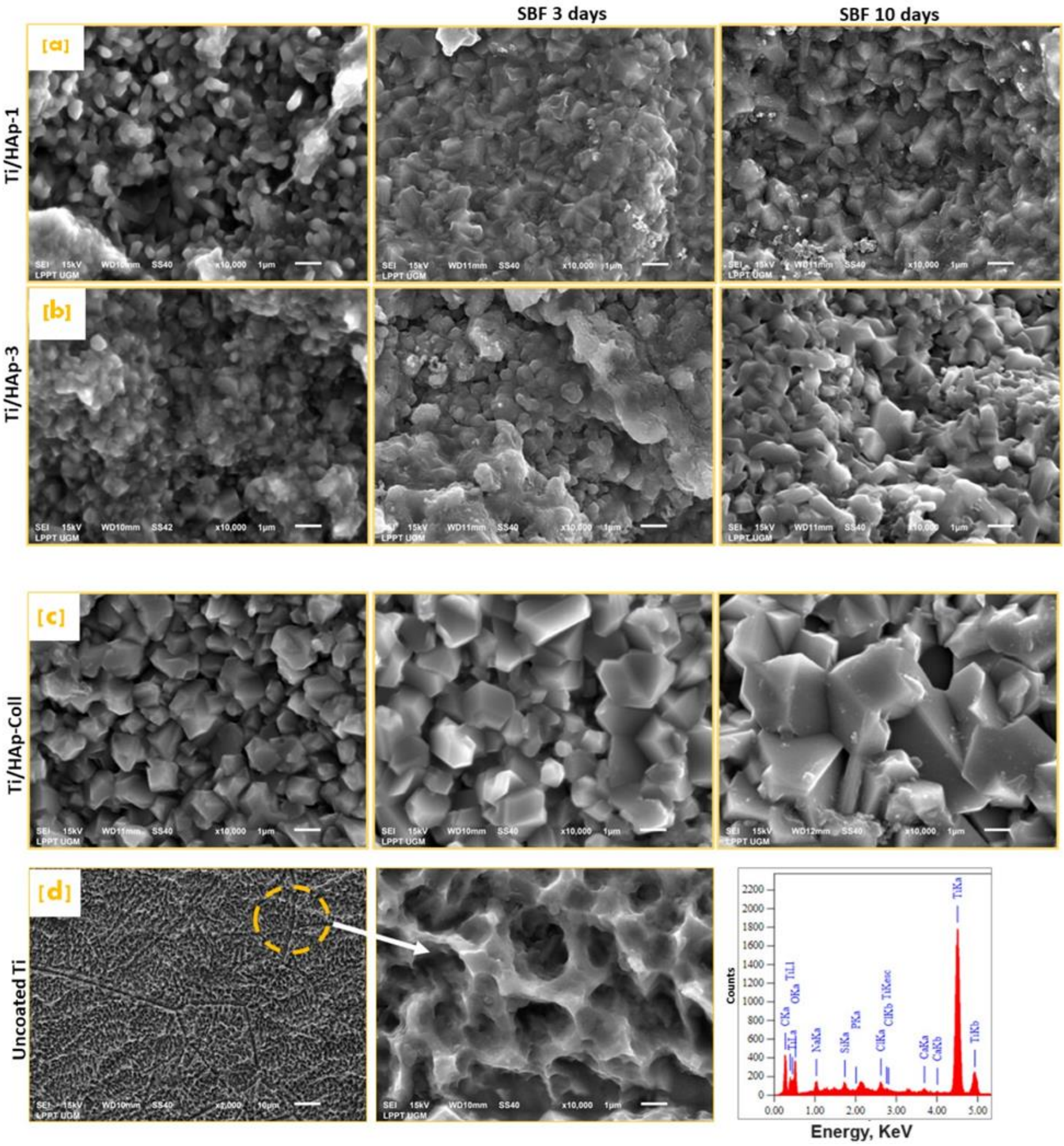

Figure 9. *Ti substrates' surface morphology both before and after SBF immersion, Ti/HAp-1 (a); Ti/HAp-3 (b), Ti/HAp-coll (c), and uncoated Ti after 3 days SBF immersion with EDS spectra (d) [43] (CC BY 4.0 Attribution)*

Table 1. *Bioactivity analysis of various materials coated with HAp*

V_{SBF} / ml*	SBF condition	Day of immersion in SBF	t_I / °C**	Materials / Powders	SBF	Ref.
50	Static	21	-	316 L / HAp	Solution used for 3-10 days	[43]
40	Dynamic	14	36.5 ± 1	254SS / HAp	Solution used for 14 days	[44]
-	-	14	37 ± 0.5	316 L SS / HAp	Freshly solution is used	[45]
700	Dynamic	-	37	SS - 316 L / HAp	every 48 hours	[46,47]
-	Dynamic	3-10	37	Ti/ HAp	Freshly solution is used every two days	[48]
150	Dynamic	7	37	HAp-C nano-composites	-	[49]

*Volume of SBF; **Incubator temperature

Electrochemical corrosion analysis

The oxidation and wear of implant materials can cause HAp coated components to corrode and produce particle debris. Irreversible material degradation from chemical reactions characterizes this electrochemical process, which can be made worse by various elements, including mechanical forces, inflammation, and constrained geometries resembling crevices. Several elements contribute to the deterioration and wear of the underlying substrate and protective layer in the case of HAp-coated materials. Thus, for efficient analysis and mitigation methods, it is crucial to comprehend the corrosive behaviour of HAp-coated materials and the factors causing this phenomenon [50].

Electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) have been acknowledged as two of the most dependable quantitative methods to investigate the mechanism of electrochemical reactions at interfaces and diagnose corrosion for biomedical applications [51]. Figure 10 shows the schematic setup of the electrochemical corrosion test.

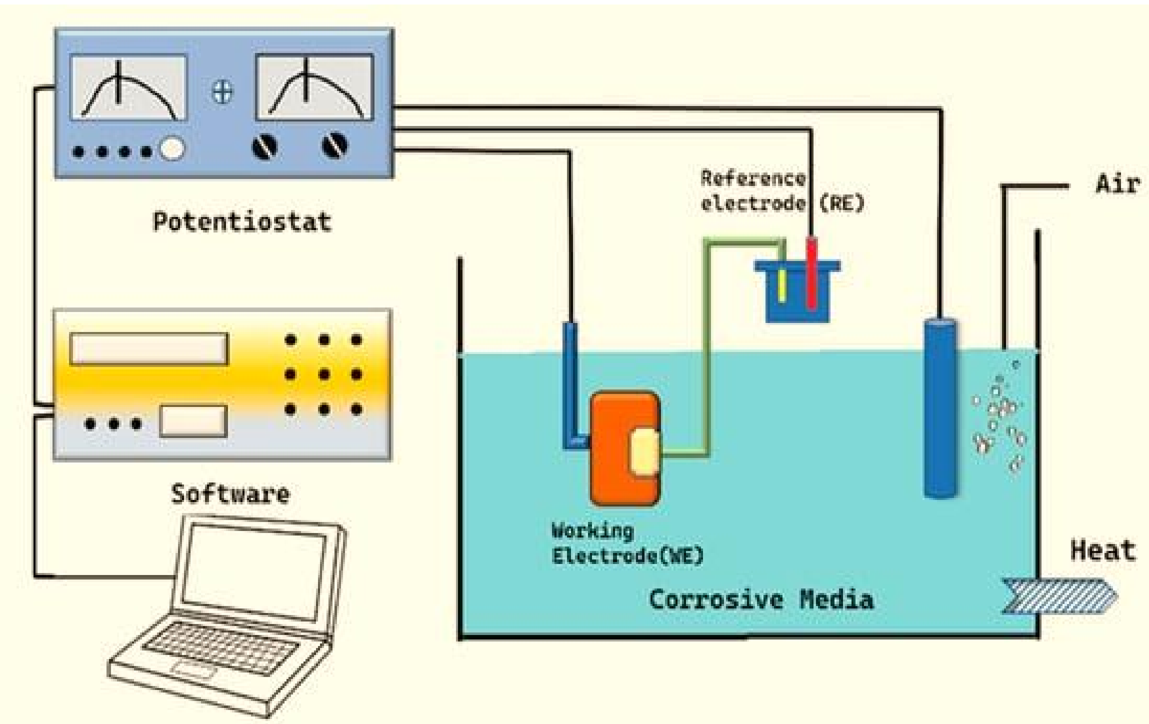

Figure 10. *Schematic diagram of the electrochemical corrosion test [52](CC BY 4.0 Attribution)*

Corrosion behaviour

The corrosion resistance of HAp coatings is an important factor to consider, especially for metallic substrates in physiological settings, even if they offer high biocompatibility and bioactivity. In addition to causing unfavorable biological reactions, corrosion can weaken the mechanical integrity of the implant. Numerous parameters, including coating thickness, porosity, and microstructure, have been shown to influence the corrosion behavior of HAp coatings. As opposed to partly melted coatings, dense and uniform coatings show higher corrosion resistance. Implants coated with HAp may behave differently in terms of corrosion depending on the substrate type and surface pretreatment used [53]. The electrochemical behavior of different materials is shown in Table 2.

***Table 2.** The electrochemical analysis of various materials.*

Biomaterial	Key features	Electrochemical corrosion analysis	Ref.
Titanium	Outstanding mechanical characteristics, frequently utilized in implants	Corrosion resistance is frequently evaluated using electro-chemical methods including electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization.	[54]
Stainless steel	High strength and corrosion resistance	The corrosion behavior under physiological settings may be assessed with the use of electrochemical techniques. Studies using potentiodynamic polarization show how resistant coatings are to corrosion.	[55]
Cobalt-Chromium	Superior resistance to wear, frequently found in orthopedic implants	The evaluation of HAp coatings' ability to withstand hostile conditions using an electrochemical corrosion study contributes to the longevity of implants.	[56]
Magnesium	Biodegradable and appropriate for transient implantation	For transient implant applications, electrochemical testing shed light on how HAp coatings on magnesium substrates corrode.	[57]
Polymers	Adaptable and appropriate for soft tissue engineering	The durability of HAp coatings on polymer substrates is crucial for biocompatibility and long-term performance, and an electrochemical corrosion study helps to understand this.	[58]

Corrosion analysis of sprayed HAp coatings

Thermally sprayed HAp coatings, including those applied by atmospheric plasma spraying (APS) techniques, have improved the biomaterials' corrosion performance with encouraging results.

The substrate material, surface preparation, and coating thickness are three important aspects that affect the corrosion resistance of thermally sprayed HAp coatings [59]. The selected substrate material, whether Ti-20%Co alloy, ASTM A36 steel, AZ31B Mg alloy, NiTi alloys, substantially affects the HAp coating-substrate corrosion behavior [60]. The corrosion resistance of the coatings in various conditions, such as saltwater and simulated bodily fluid, can also be influenced by surface roughness and the presence of nanoparticles like ZnO or TiO_2 inside the HAp coating. Critical factors influencing the coating's overall effectiveness and ability to withstand corrosion are the HAp layer's thickness and sintering temperature. Improved corrosion protection has been proven by thicker and denser sintered HAp coatings [61].

The corrosion resistance of thermally sprayed HAp coatings is commonly assessed using standard testing techniques such as polarization resistance measurements, electrochemical impedance spectroscopy (EIS), and salt spray testing (ASTM B117). These techniques offer a thorough evaluation of the coating's functionality in many settings [62].

Influence of corrosion behavior on biomaterial performance

Because of the chemical processes between the material and its surroundings, corrosion is an electrochemical process defined as irreversible material degradation. Because metallic biomaterials' corrosion behaviour affects their functioning, sustainability, and biocompatibility, it is frequently evaluated for quality control and failure analysis. It has been proposed that biocompatibility increases with corrosion resistance.

Although metallic biomaterials have a strong corrosion resistance, it has recently been suggested that implanted biomaterials will begin to physically deteriorate after 12 to 15 years due to electrochemical processes. Consequently, when designing and choosing biomaterials for biomedical purposes, corrosion is thought to be a significant consideration. Because of the body's aqueous liquids, the implants that have been inserted have difficulties with corrosion behaviour because of electrochemical reactions. The most important elements of bodily fluids that influence how metallic implants corrode are chloride, pH, and dissolved oxygen. Sulphur, hydrogen, potassium, sodium, magnesium, and calcium ions are among the major cations found in bodily fluids. However, significant anions consist of phosphate, hydroxide, chloride, sulphate, and bio-carbonate. As far as metallic implants are concerned, the dissolved salts have the greatest impact on how they corrode [63].

Mechanical integrity of coated implants

The hydroxyapatite (HAp) coating considerably improves the mechanical integrity of implants when compared to those that are not coated. Mechanical integrity is favored by the coating's ability to lower the rate of corrosion, strengthen bonds, and slow down decomposition. The localized corrosion of the alloy is greatly reduced by HAp coatings, which improves the mechanical integrity of the alloy while it is in use. Coated implants have better qualities than bare metallic implants as well. Additionally, the coating enhances osteogenesis and exhibits improved osteoinductive and osseointegration activities by promoting hard-tissue differentiation, macrophage polarisation, and the production of new bone. Moreover, quick osseointegration and long-term stability have been linked to HAp coating, which has produced encouraging clinical outcomes like higher implant stability and improved survival rates. It is imperative to consider plausible reasons for the failure of HAp-coated implants, such as inadequate adhesion between the coating and the metal, HAp coating deterioration due to bodily fluid contact, fatigue cracks, delamination, fretting wear, and instability of the HAp film. Complications include implant loosening, non-union, bacterial infections, and material deterioration from mechanical pressures can result from these failure types [64].

Strategies for enhancing bioactivity and corrosion resistance

To increase the bioactivity and corrosion resistance of thermally sprayed HAp coatings, several tactics have been investigated. These include adding bioactive chemicals, changing coating compositions, improving spray settings, and post-treatment methods, including surface modification and heat treatment. Furthermore, research has been conducted on sophisticated coating designs, including gradient and multilevel structures, to enhance the mechanical and biological performance of HAp coatings [65].

A wide range of implant applications have significantly used metallic biomaterials, including titanium alloys, cobalt-based alloys, and stainless steel, in the medical profession because of their superior mechanical qualities and compatibility with physiological environments. The main issue with these metallic implants is that their chemical makeup does not exactly match human bone, which might result in poor bone-implant integration and implant failure.

HAp coatings have been widely applied to metallic implants via thermal spraying techniques, such as plasma spraying, among other coating methods. Using these methods, a coating layer is created by melting and rapidly moving HAp powder particles in the direction of the substrate. However, weak adhesion strength, large porosity, and the possibility of phase breakdown during the high-temperature deposition procedure frequently restrict the performance of these thermally sprayed HAp coatings [66].

Improving adhesion strength

The strength of adhesion between the hydroxyapatite and the metallic substrate plays an integral role in the lifespan of an implant. In this case, the application of coupling chemicals, including titanium, proves to be an efficient way to enhance the bonds.

Moreover, these chemicals cause the chemical composition of the coating and substrate to realize a more potent chemical bond. When working with titanium, the element contributes to the development of a durable interfacial layer, which significantly improves mechanical interlocking and increases adhesion strength overall. This is a requirement for implant parts to remain strong and intact under physiological conditions. The result is the elimination or reduction of the coating's risks of falling off or peeling, which keeps HAp attached to the substrate. This ensures the maintained composure of the formation throughout its life cycle. This, in turn, is necessary for the implant's high performance and reliability. Thus, coupling chemicals, where titanium can be named as an example, is a viable method of designing durable implants [67].

Controlling coating microstructure

The HAp coatings are the most important factor in determining their bioactivity and corrosion resistance in the microstructure. Thus, the HAp microstructural characteristics also include some attributes that have a notable effect on the behavior of these coatings on orthopedic and dental implants at the porosity, crystallinity, and phase composition of HAp. As low porosity is desirable for HAp coatings in terms of strength, high porosity levels may cause a mechanical failure of the coating and increase the chances of its corrosion, as the porous structure supports (PSS) fracture. In the case of HAp crystallinity, on the other hand, higher levels have been observed to be more conducive to the bioactivity and structural stability of the coating. Among the methods to improve the quality of HAp coatings produced with PSS, modifying the deposition methods commonly used on a wide scale makes them ready for utilization in advanced deposition methods such as suspension plasma spraying (SPS) and high-velocity suspension plasma spraying(HVSPS). SPS and HVSPS both involve the injection of a suspension of fine HAp powder in a liquid medium into a plasma jet [68].

These techniques provide a controlled environment for deposition, leading to a decreased porosity in the coatings due to inadequate sintering. The rapid solidification and high kinetic energy associated with SPS and HVSPS resulted in a more homogeneous, crystalline structure. The improved crystallinity exhibited by the SPS and HVSPS coatings makes them more bioactive. They have a more favorable surface topography for bone-forming cell attachment and a slower rate of dissolution in the biological environment. Moreover, because they are less porous, they are more resistant to fluid infiltration, making them more resistant to corrosive action on the metallic substrate [69].

Incorporation of reinforcing materials

Coatings with such reinforcing components have already been widely explored. Although TiO_2 has not been substantially utilized in coatings, some authors suggest that, by increasing the hardness and wear resistance, TiO_2 can dramatically improve coating durability. Carbon nanotubes increase the strength and flexibility of coatings, making them more durable and tougher. ZrO_2 makes the structure of the coating more rigid by enhancing its heat resistance and increasing the hardness. These materials strengthen membranes and improve them in terms of environmental resistance along with several other beneficial properties. For difficult conditions, oxide systems can provide coatings resistant to chemical attack and corrosion. Additionally, CNTs can enhance a coating's ability to withstand mechanical stress and delamination. These substances also contribute to the adhesion of the coating to the substrate. This is crucial for adhesion-seeking applications since the film may peel off or collapse under working stress without high adherence [70].

Post-deposition treatment

Post-deposition treatments, annealing, and sintering play a vital role in optimizing the properties of thermally sprayed hydroxyapatite coatings. These processes increase crystallinity, which is essential for enhancing the bioactivity of coatings because better-crystallized hydroxyapatite provides a surface that is more suitable for bone cell adherence and proliferation. Furthermore, increased crystallinity also increases the adhesion strength, such that the coatings are more firmly attached to the substrate in physiological conditions. Annealing involves heating the coatings to a specific temperature below the melting point at which atoms diffuse and internal stresses are relieved. This process refines the microstructure in such a way that porosity is reduced and density is increased. Sintering is done at higher temperatures, at which the bonding between particles is facilitated by densifying the coatings, where atom diffusion promotes the elimination of voids and density is further increased. Better crystallinity, adhesion strength, and density collectively result in better bioactivity and corrosion resistance. Hence, enhanced bioactivity ensures that the HAp coatings adequately allow bone integration, while better corrosion resistance ensures that the aluminum substrate does not degrade in the biological environment. Therefore, post-deposition treatments significantly enhance the performance and service life of thermally sprayed HAp coatings [71]

Future scope

In the biomedical field, thermally sprayed HAp-based coatings are valued for their bioactive qualities and resistance to corrosion. To further progress in various fields, such as biomedical engineering, aerospace, automotive, and marine industries, researchers are actively looking for ways to improve these coatings [72].

Future research endeavors might focus on enhancing the bioactivity of HAp coatings to enhance the longevity and functionality of biomedical implants. Increased integration with biological systems will be made possible by this. Investigating how to modify and adjust these coatings to meet specific industrial needs, whether related to mechanical strength or corrosion resistance [73].

Due to the advent of sophisticated characterization techniques, researchers are now able to investigate the intricate relationships between structure and property at the nanoscale, providing valuable insights for the optimization of coating performance. Additionally, the quest for multifunctional coatings is an exciting area for future study because they offer corrosion resistance and bioactivity in addition to other characteristics like antibacterial or drug transport properties.

The application of these coatings in various industries will rise with the incorporation of sustainability and eco-friendliness into the synthesis processes and the assessment of their environmental impact. Cutting-edge technologies like additive manufacturing and nanotechnology can be combined by researchers to push the frontiers of innovation and open new potential for HAp-based coatings. In summary, there are numerous opportunities to advance our understanding and use of thermally sprayed HAp in the future [74].

Conclusion

The evaluation of the bioactivity and corrosion analysis of HAp-based coatings includes a detailed investigation of the behavior of corrosion and thermal spray coating features. The observation by other studies that HAp coatings increase the material's resistance to corrosion validates the results.

Studies on the development of HAp coatings, particularly for orthopedic applications, have shown how important it is to understand cold spray techniques to carry out HAp deposition. The potential applications of these coatings in biomedical implants are increasing continuously due to ongoing research activities. The chemical face and surface topology, as well as their phase stabilities of thermally sprayed HAp coatings, significantly affect bioactivity. Osteogenic and bone-bonding properties can be improved by adding more bioactive elements such as Sr, Mg, and Zn. The essential elements for the enduring integration of bioimplants in the human body are advised to be the biological functions and the properties of the transformed surface. To guarantee the Biocompatibility and biofunctions of biomaterials, HAp-based coatings are necessary. This leads to superior osseointegration and quicker formation of the hard tissues.

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