

# EFFECT OF VARIOUS ADDITIVES ON MECHANICAL AND BIOLOGICAL PROPERTIES OF HYDROXYAPATITE COATING

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Abstract- The hydroxyapatite (HAP) coating is the most commonly used in the biomedical implants due to its excellent biocompatibility and bio-stability. However, the hydroxyapatite coating has low fracture toughness and wears resistance which can results in earlier implant failures. Although the hydroxyapatite coating is nontoxic and bioactive but it lacks in antibacterial activity can cause infection. Infection may results in second revision surgery to remove the implant. To address this problem hydroxyapatite is doped with various additives. In this review paper, the approach was to explore the effect of various additives on the hydroxyapatite coatings.

Keywords: Hydroxyapatite (HAP), Biocompatible, nontoxic, reinforcement, implants.

## **1. INTRODUCTION**

The demand of the orthopedic implants around the world has increased over the past few decades with the increase in world population and accidents rates. As orthopedic implants used are mainly made up of metals so the biological interactions of metallic implant with body tissues is very low. Also the implants are in regular contact with the body fluids are susceptible to corrosion [1]. The body fluid contains various anions (Cl<sup>-</sup>, HCO3<sup>-</sup>, and HPO4<sup>-</sup>), cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>+2</sup>, Mg<sup>+2</sup>) and dissolved oxygen [2]. So often these metallic implants are coated with ceramics materials to enhance the biological response.

The surface scientist plays the crucial role in the area of the biomedical engineering. It is the surface of the implants that interacts with the body fluid. The biological reactions are taking place at the interface so tailoring the surface chemistry of an implant can improve the efficiency of an implant [3]. So from the implant design aspect the surface modification is the most investigated [4].

Hydroxyapatite (HAP) is brittle bioactive ceramic material that cannot use as an implant in bulk form. So the hydroxyapatite coating is mainly used over metallic substrate. The deposition of hydroxyapatite coating over metallic substrate combines the advantages of the metal for load bearing and hydroxyapatite coating for the biological performance [5].

The main limitation of the hydroxyapatite coating is poor fracture toughness and the wear resistance. Also it has lack of antibacterial activity that can affect the long term stability. The most suitable method to overcome this problem is reinforcing the hydroxyapatite with second phase material. Researchers have explores various reinforcing material such as hard ceramics, polymers etc. The ideal reinforcing material is one which increases the fracture toughness and wears resistance of hydroxyapatite coatings with very minimum reinforced phase **[6, 7]**.

## 2. EFFECT OF VARIOUS ADDITIVES ON HYDROXYAPATITE COATING

Bone is composite material that consists mainly of 70% hydroxyapatite, 20% collagen and rest 10% water. The hydroxyapatite mimics the natural bones, so it is used for the various biomedical applications such as bone fillers and tissue engineering scaffolds, used as a coating material for orthopedic and dental implants and the drug delivery systems[8]. Amongst them, most important application of the hydroxyapatite is preparation of implant coating. As discussed earlier there are some limitations of pure hydroxyapatite coatings so by tailoring the composition of various additives, surface engineer can designed the hydroxyapatite composite coatings for various clinical applications.

## 2.1Effect of the Silicon Dioxide (SiO<sub>2</sub>)

Silicon dioxide in glassy form has been used from thousands of years. Silicon oxide based materials are studied extensively from past several years[9]. Silicon is the essential element for the growth and development of the bones, teeth and some invertebrate skeletal parts. The addition of silicon in the hydroxyapatite increases the rate of formation of apatite layer physiological media [10]. The addition of small percentage of silicon dioxide in hydroxyapatite improves the invivo bioactivity and it also promotes the early bone ingrowth. It ensures a strong bioactive bond between the implant and the bone. Improvement in Surface adhesion is also observed in the silica doped hydroxyapatite [11].

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Morks [12]studied the effect of silica content (10 wt% and 20 wt %) on the Ha-silica coatings deposited by gas tunnel- type plasma spraying process. The results showed that the Ha-silica (10 wt% and 20 wt %) coatings have dense structure than pure hydroxyapatite coatings. It was observed that with the increase in silica content the coatings become denser, harder and improved in abrasive wear resistance. Also the presence of silica improved the bonding strength of the Ha-silica Coatings. Xu et al. [13]deposited the silicon doped hap with the help of plasma sprayed coating process on titanium based alloy. The hap was doped with 1 wt%, 2 wt% and 5 wt% silicon oxide. To improve the adhesive strength the substrate was pre-heat treated to 250°C with the help of plasma prior to coating. It was observed that with pre-heat treatment, the silica has improved the hardness, modulus and adhesive strength of coatings.

#### 2.2 Effect of the Titania (TiO<sub>2</sub>)

Owing to the high specific strength and excellent corrosion strength, titania is extensively used for the orthopedic and dental applications. Also the good permeability and high biocompatibility of titania enhance the cell viability [14]. The titania is widely used for the photocatalytic application. The titania is quite helpful in killing the different microorganisms such as bacteria, viruses, fungi, protozoa, algae etc [15]. The composite of hydroxyapatite and titania has not any toxic effects as confirmed by the cytotoxicity and cytocompatibility tests. The HAP/TiO<sub>2</sub> composite is excellent in antibacterial applications and environment purifications. It has ability to adsorb bacteria and organic materials and also helpful in catalytic decompositions of biomaterials, such as proteins and lipids[16]. The addition of titania significantly increases the adhesive and cohesive strength of hydroxyapatite [17].

Yugeswaran et al. [18] prepared the HA-nanostructured  $TiO_2$  composite coatings reinforced with 10 wt%, 20 wt% and 30 wt %TiO<sub>2</sub> using gas tunnel type plasma spraying torch under optimized spraying conditions. It was observed that with the increase in the weight percentage of the nanostructure  $TiO_2$  in the composite coatings there is significant increase in the microhardness, adhesive strength and wear resistance. Also the bioactivity results showed that the composite coating surface has good bioactivity and the cytocompatibility. Gaona et al. [19]deposited the HA-nanostructured  $TiO_2$  composite coating having (80 wt%, 90 wt %) nanostructured  $TiO_2$  using high velocity oxy fuel coating process on titanium based alloy. The x-ray diffraction results reveals that there is no chemical reaction place between the HA and  $TiO_2$  phase during the spray process. Further as the weight percentage of titania increases, its addition improves the bond strength and hardness values of the coatings.

#### 2.3 Effect of the Alumina $(Al_2O_3)$

Alumina  $(Al_2O_3)$  is bioinert material.Owing to excellent wear and corrosion resistance, alumina is widely used for load bearing applications.  $Al_2O_3$  have high elastic modulus and compressive strength. It improves the mechanical properties of hydroxyapatite and is also helpful in retained the biocompatibility, but addition of higher percentage of  $Al_2O_3$  decreases the fracture toughness of HaP-Al\_2O\_3 composite [20]. The 20 vol. %  $Al_2O_3$  addition in the form of platelets increases the fracture toughness by four times. The addition of  $Al_2O_3$  also improves the bending strength of the HAP composite[21].

Mittal et al.[22]deposited thehydroxyapatite composite coating reinforced with alumina (10 wt%, 20 wt% and 30 wt %) with plasma spray coating process on titanium based alloy. It was observed that in the HaP-Al<sub>2</sub>O<sub>3</sub> composite coatings that there is increase in micro hardness, tensile strength and wear resistance with increase in alumina content. In another studySingh et al.[23] prepared the pure HA coating and HA reinforced with 10 wt. % ( $80Al_2O_3-20TiO_2$ ) coating by plasma spray process deposited on Ti<sub>6</sub>Al<sub>4</sub>V alloy. The reinforcement increased the tensile strength, also marginal increase in microhardness and surface roughness was observed. Further both the pure and reinforced coating shows excellent corrosion resistance.

#### 2.4 Effect of the Carbon Nanotubes(CNT)

Carbon nanotubes are widely used in the field of science, technology, engineering and medicine. The applications of the carbon nonotubes in medical field include drug delivery, for the construction of biosensors or material engineering [24]. The carbon nanotubes have excellent mechanical properties and biocompatibility. It can be used as a reinforcing phase to strengthen the hydroxyapatite coatings [25].

Balani et al. [26]Deposited the pure coating and composite hydroxyapatite coating using Ha-4 wt% CNT with the help of plasma spray coating process on titanium based alloy. It was observed that the composite coating has 56% more fracture toughness and 27% enhance in the crystallinity than pure hydroxyapatite coating. Further the cell culture studies confirmed the composite coating promotes cell growth and proliferation. Tercero et al. [27] developed the bioceramic composite coating Ha-20% Al<sub>2</sub>O<sub>3</sub> shows 158% improvement in fracture toughness, whereasHa- 18.4% Al<sub>2</sub>O<sub>3</sub>-1.6 wt% CNT showed an improvement of 300% in fracture toughness. The reinforcement provided by the carbon nanotubes is with the help of reber mechanism. It was observed from Human fiber osteoblast cell growth studies that the Al<sub>2</sub>O<sub>3</sub> retained its bio-inertness, CNT, its bioactivity while the biocempatibility of the composite coatings remains intact.

### 2.5 Effect of silver (Ag)

The post surgical infection is one of the major problems of the biomedical field. Mostly, these infections are arises due to the orthopedic implants. These orthopedic implants provide sites for the bacterial adhesion which leads to severe pain, bone tissue loss and eventually results in the revision surgery. Numerous studies pointed out that the silver has strong antimicrobial property[28]. Invitro studies also indicated that the inclusion of silver, copper and zinc ions in the coating can avoid the adhesion of bacteria [29]. The silver is nontoxic to human organism in low concentrations. The inclusion of silver to hydroxyapatite coating can provide good antibacterial properties to the coating [30].

In a studyFielding et al.[31] to improve the antimicrobial property of the implant coating, hydroxyapatite was doped with 2% Ag<sub>2</sub>O. Also to counteract the potential cytotoxic effect of silver, 1wt% strontium (Sr) was also added. The composite coating HA-2% Ag<sub>2</sub>O-1wt% Sr was obtained by plasma spray process. Post heat treatment was also done at 800°C. The coating was tested against the pseudomonas aeruginosa to test the antibacterial efficacies. It was observed that the composite coating contained Ag<sub>2</sub>O have highly efficient against bacterial colonization. In another workLiu et al.[32]synthesized an Ag incorporated HA nanocomposite using chemical reduction method. To study the antibacterial effect of nanocomposite strain Escherichia coli was used. It was observed during the In vitro bacterial adhesion study that there is significant improvement in the antibacterial property of silver containing HA.

### **3. CONCLUSION**

The reinforced second phase material such as ceramics improves the fracture toughness and wears resistance but the numerous studies pointed out that bioactivity of the composite hydroxyapatite coating is less than the pure hydroxyapatite coating. The ideal reinforced second material should be such that it significantly improves the fracture toughness and wear resistance with minimum reinforced phase. All the bioceramic materials discussed here in this review have potential to be used as a second phase reinforced material. The mechanical and biological properties of the composite coating can be tailored by controlling the composition of these reinforced second phase materials. Further research is needed to explore the application of second reinforced phase.

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