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## Brief Review on Corrosion Behavior of Hydroxyapatite Coatings.

Durairaj RB<sup>1</sup>, and Ramachandran S<sup>2\*</sup>.

<sup>1</sup>Research scholar <sup>2\*</sup>Professor <sup>1,2\*</sup> Faculty of Mechanical Engineering, Sathyabama university, Chennai, Tamil Nadu, India.

### ABSTRACT

Hydroxyapatite is a bioactive and biocompatible ceramic material with major composition of calcium and phosphorous which is a primary constituent of human bones. It has a prominent role in the replacement of bone cement and other corrosion protecting materials in implant surgeries. It also helps in the formation of osteoblasts cell (Mesenchymal stem cells) and tissues with strong adhesion and dense structures over the implant location. In general Hydroxyapatite cannot stand alone as an implant material due to its poor mechanical properties. It can be employed as coating materials or in the form of reinforcement with other biomaterials. In this review we have summarized about the Corrosion characteristics of hydroxyapatite coatings over titanium (Ti), surgical grade stainless steel (SS316 L) and Magnesium alloys substrates in simulated body fluid solution (SBF). The ionic concentrations and PH (7.40) of SBF solution are made equal to the human blood plasma.

**Keywords:** Hydroxyapatite; Osteoblasts; Corrosion Behavior; Simulated body fluid; Blood plasma.

*\*Corresponding author*

## INTRODUCTION

Biomaterials are synthesized to perform in body environment to substitute for the damaged bones and tissues. They are expected to withstand the loads offered by the body and create corrosion resistance to body fluid [1, 2]. Hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  are chemically similar to composition of human bones with osteoconductive nature. Generally pure HA exhibits lower mechanical stability and quick dissolution in simulated body fluid solution [3, 4]. T. Laonapakul et al reported that the implant of pure HA coatings may occur frequent fracture in live body environment over time period. This can be overcome by the introducing bioactive materials as reinforcement [6, 7]. Vidakhalili et al reported that the nano indentation analysis of hydroxyapatite and silicon-multiwall carbon nano tube composite coating showing highest elastic modulus of 45.8Gpa which is greater than bone tissue of 30Gpa. [5].

X. Feng Juan has reported that reinforcement of Si to HA coatings improve bioactivity and this Si material plays major role biological processes of human body [8]. F.Chen reported about the introducing of carbon nano tubes (CNT) will improve the mechanical properties of the coatings and it has a similar morphology of nano-scale collagen fibers of natural bone tissues [9]. Y- H. Jeong reported that more adhesion on HA has been achieved on nano tubular oxide layer when compared to air formed oxide layer in the attempt of adhesion improvement through interlayer of HA.[10-11]. The introduction of oxygen and ammonia during the microwave plasma enhanced chemical vapor deposition of HA process will improve better adhesion of the coatings over the substrate [12]. L.Sun et al reported crystalline form of HA has slower degradation in vivo experimentation compared to amorphous structured HA and protect the coatings from corrosion for a longer period [13]. Grabmann et al observed that there is a decrease in adhesive strength of the coating in simulated body fluid solution in an immersion period of 14 days [14].

Yang et al reported about the improvement in adhesive strength of the HA coatings with plasma spray coating process and reduced the residual stress of the coatings [15]. Rackngarm et al reported that the Ti/HA bonding has improves the cracking resistance with positive stress ratio [16]. Yuichi otsuka et al experimented on HA coatings and reported that the residual stress of the coatings can overcome by treating the samples with 650 ° C for 1 hour period in atmosphere furnace followed by air cooling [17]. K.Izumi et al reported that sol gel is used to achieve required coating thickness and at low heat treatment temperatures [18]. D.Gopi et al reported that cathodic electro deposition (CED) is more suitable for low deposition temperature, and helps in formation of coatings in complex shapes and porous substrates. [19 - 22]. Cleries et al has not observed a degradation of crystalline HA coatings over the immersion of 120 hr period in Simulated body fluid solution [23 - 24]. Presence of HA coatings will decrease the release of hydrogen up to 75 to 78% for the immersion period of 240 hrs in Simulated body fluid solution [25]. This review gives the summary about the HA deposition over various substrates of biomaterials and their corrosion behavior in Simulated body fluid solution. This corrosion property will helps in calculation of implant life in the period of replacement inside the body. Immersion testing of the samples in SBF is similar to testing the sample in vivo. The ionic concentrations and  $P_H$  are identical.

### Corrosion characteristics of Hydroxyapatite in simulated body fluid

Kokubo protocol of simulated body fluid solution helps in the identification of in vivo Corrosion behavior of the HA coatings. This solution can be prepared by Reagent – grade sodium chloride (NaCl) , Sodium hydrogen carbonate ( $\text{NaHCO}_3$ ) , Potassium chloride (KCl) , di-potassium hydrogen phosphate trihydrate ( $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ ), Magnesium chloride hexahydrate ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), calcium chloride ( $\text{CaCl}_2$ ) and sodium sulphate ( $\text{Na}_2\text{SO}_4$ ), were dissolved in to De Ionized water [35].

Conor.F.Dunne et al performed immersion and electrochemical analysis for the HA coated magnesium alloys in phosphate buffered saline solution. The temperature of the system has maintained to 37°C for 10 days. This process is examined through the percentage of hydrogen evolved and percentage of magnesium dissolved in the solution. It was reported that the hydrogen evolution for the samples observed 56 ml/cm<sup>2</sup> after 240 hrs. Also the HA coated magnesium alloys exhibit better corrosion resistance during this process. They also performed this corrosion examination for the uncoated samples, but the coated samples have less hydrogen evolution than uncoated. The presence of HA layer as coating has reduced the release of hydrogen by 34% during the immersion. [26 – 30]. The presence of HA over the substrate will act as a barrier to avoid the

transportation of electrons and ions between substrate and electrolyte solution. This will reduce the rate of corrosion of the implant.[31 – 34 ].

Yuichi Otsuka et al has conducted corrosion examination for HA coated Ti substrates using KuKbo's SBF solution technique [35]. The samples were immersed in simulated body fluid solution for 1 week and the temperature was maintained to 37°C. The solution was changed periodically in the interval of two days. The delaminating behaviors of the coatings are examined with loading frequency of 0.02 Hz. It is observed that the delaminating is not exceeded greater than 1 mm for  $5 \times 10^6$  cycles. Also the delamination propagation rate of HA coating became higher in simulated body fluid solution. [37 – 41]

Yakup say et al conducted corrosion examination for HA – SiO<sub>2</sub> composite coatings over Stainless steel substrates using potential dynamic polarization. The corrosion cell was maintained with temperature of 37°C and silver chloride electrode is used as a reference electrode and platinum has been used as a contrary electrode. It is observed that the cracks are formed over the HA layer and the addition of SiO<sub>2</sub> has decreased the pore density and reduced the formation of corrosion in the coatings. [ 42 – 46 ] Laonapakul et al reported that presence of HA coatings are not prone to corrosion resistance as expected because of the presence of the porous structure. These pores are act as zones where the electrolytes were remains and the internal sides of the pores are filled with the oxides of the corrosion products. The addition of SiO<sub>2</sub> will cover the pores and act as a barrier for the access of the corrosion products. Also the local corrosion of the surface creates dimple in the coatings [47 – 51].

Yong Huang et al has conducted corrosion resistance examination on strontium and manganese co-substituted HA ceramic coatings over Ti substrates. They were performed the potential dynamic polarization test with LK2005A electro chemical system. The corrosion resistance of SrMnHA coated samples is more when compared to uncoated and HA coated samples in simulated body fluid solution. This results are similar to the ionic doped HA deposition over the Ti substrates [52-54]. The uniform deposition and surface protection of SrMnHA coatings helps in achieving the maximum corrosion resistance. The reduced grain size of the particles has greater role in the formation of barrier to the electron transfer from the substrate to electrolyte [55 – 58].

Krai Kulpetchdara et al conducted corrosion examination on thermally sprayed Nano HA and commercially available HA powder over stainless steel substrates in simulated body fluid solution. Over a period of 14 days, it is observed that the coatings were covered with nano crystalline layer with different surface morphology was identified. The cauliflower like precipitates is observed in the scanning electron microscope image. [59 – 62]. The phenomenon of the formation of the precipitate layer will shows the formation of bioactivity over the coatings. [63 – 65].

Kean – Khoon Chew et al conducted experiment on HA coated stainless steel 316 L using Electrophoretic deposition method. The corrosion behavior was examined by the electrochemical examination using simulated body fluid and three electrode system with saturated calomel electrode as a reference electrode. For the open circuit potential of applied voltage 40 V shows greater corrosion resistance of HA deposited SS 316 L. this is due to formation of thick coating during the electrophoretic deposition [66 – 70].

Dinh Thi Mai Thanh et al are conducted corrosion test on HA coated SS316 L in simulated body fluid solution. It is observed that in five days of immersion calcium and phosphorus ions polarization occurs from SBF solution to cavities of HA makes the local concentrations of ions relatively high [ 71 – 73 ] .

#### SUMMARY

It is summarized that deposition of pure HA as a corrosion protection layer will not create the resistance for the corrosion as expected. This can be performed to some extent by different deposition techniques with dense coatings. Also the structure of the HA (Crystalline or amorphous) matters a lot in the protection layer formation. The porous coating may led to more corrosion rate. In case open circuit potential examination in simulated body fluid the corrosion products will get in to these pores and increase the corrosion rate. Reinforcement of Si, CNT with HA forms a composite and close the pores in HA deposition. This composite will act as a barrier for transfer of ions between the electrolyte and the substrate of the coating. In some of the experiments it is observed the formation of bioactive layer over the immersion period of 14 days in simulated body fluid solution. It is concluded that HA coatings for the implants with suitable deposition

process and reinforcement will create the anti - corrosive barrier for the substrates and improves the bio - compatibility of the implant.

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