Behavior of Thermally Sprayed Bioceramic Coatings after immersion in SBF: A Review

Amardeep Singh1*, Gurbhinder Singh2, Vikas Chawla3

1Punjab Technical University, Kapurthala, Punjab, India, 144601, E-Mail: amardeepkang@gmail.com

2Guru Teg Bahadur Khalsa Institute of Engineering & Technology, Chhapianwali-Malout, Punjab, India, 152107, E-Mail: gurbhinder@yahoo.com

3DAV College of Engineering & Technology, Kanina, Mohindergarh, Haryana, India, 123027, E-Mail: vikkydmt@gmail.com

Abstract

Significant research has been devoted to the development of hydroxyapatite (HA) as a coating material for metallic biomaterials used in bioimplants where the biocompatibility is provided by HA while the mechanical properties of the implant are confirmed by the metallic substrates. The in vitro tests of these coatings have conducted by soaking in simulated body fluid (SBF) solutions to evaluate the change in morphology and mechanical performance. The review shows that the mechanical properties like bond strength, wear resistance, microhardness and young’s modulus etc. of pure HA coatings found to diminish more after soaking in SBF compared to reinforced HA coatings, but it remains constant for the heat treated coatings. The dissolution of secondary phases in SBF is evident after immersion and the surfaces of composite coatings have completely covered by carbonate containing apatite which shows the good bioactivity of composite HA coatings.

Keywords: Hydroxyapatite, Bioimplants, Bioceramic, SBF

1 Introduction

Surmenev (2012) reported that surgical stainless steels and titanium and its alloys are metallic materials which are mainly used for orthopedic implants due to their high strength and toughness. However, these metallic biomaterials are subjected to corrosive attack by body fluids which results into release of harmful metallic ions effecting adversely to the surrounding tissues as stated by Mudali et al. (2003). Moreover, these biomaterials are in general not adequately bioactive and some suitable surface modification is usually required to improve their bioactivity. In view of these, implant materials are commonly coated with hydroxyapatite \((\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2)\) a bioceramic which is chemically similar to the mineral component of bones and teeth as assessed by Arcos et al. (2004). The HA coating therefore acts as a barrier to the release of metallic ions and at the same time enhance the bone bioactivity by virtue of its chemical constituents as revealed by Cook et al. (1992).

Fernandez et al. (2007) reported that hydroxyapatite coatings for orthopedic implants were introduced around two and a half decade before to enhance fixation between bones and implant. Several techniques can be used to deposit HA coatings on the metallic bio-implants surfaces such as micro-arc oxidation used by Chen et al. (2006), sponge replication process by Lee et al. (2009), electrostatic spray deposition by Sander et al. (2006), sol-gel process by Liu et al. (2002), electrophoretic deposition by Sridhar et al. (2003), ion beam sputtering by Wang et al. (2001), rf-magnetron sputtering by Nelea et al. (2003), pulsed laser deposition by Wang et al. (1997) yet the most of the present day researchers are interested to deposit HA coatings by using thermal spray techniques as used by Li et al. (2002), Kweh et al. (2000), Gledhill et al. (1999) and Singh et al. (2011) because these processes are fastest methods to deposit thick and dense HA coatings with good adhesion with the substrate. Plasma spray is the only thermal spray process which is approved clinically by Food and Drug Administration (FDA), USA due to its excellent coating properties as compared to other coating techniques. But apart from these benefits, some common problems are also associated with thermal spray techniques.

The high temperature in thermal spray leads inevitably to changes of the degree of crystallinity of HA coatings i.e. the formation of foreign phases such
as α-and/or β tricalcium phosphate (α-TCP, β-TCP), tetracalcium phosphate (TTCP), CaO, amorphous calcium phosphate (ACP) and oxyhydroxyapatite (OHA) as reported by Li et al. (2002) and Gross et al. (1998). Gu et al. (2003) investigated that these metastable phases greatly influence the mechanical properties as well as the biological behavior of the coating system because these phases dissolve quickly in body fluid environments. It is recognized that the contents of secondary phases and crystallinity are important factors to be considered for the persistence of long-term stability of HA coatings in aqueous environments.

Therefore in this review an attempt has been made by authors to ascertain the effects of simulated body fluids on morphological changes and mechanical performance of pure and reinforced HA coatings.

2. Morphological Changes

Dissolution behavior of pure HA and composite coatings reinforced with different wt% of zirconia (ZrO\textsubscript{2}) and mol% of yttria were studied after incubation in SBF by Chang et al. (1997). The dissolution rate of impurity phases such as TCP, Ca\textsubscript{5}P\textsubscript{2}O\textsubscript{8} and CaO was higher after immersion in case of pure HA coating compared to ZrO\textsubscript{2}/HA composite coatings. The slower dissolution rate of composite coatings was attributed to the addition of ZrO\textsubscript{2}, because the un-dissolved ZrO\textsubscript{2} may reduce the contact of effective HA surface with SBF. Significant morphological change was observed in pure HA coating as the surface of the coating became flat after 20 days of immersion in SBF, whereas ZrO\textsubscript{2}/HA composite coatings exhibited little apparent morphological change after immersion. The similar results are elucidated by Li et al. (2009).

It has stated by Weng et al. (1997) that the as-received and heat treated (at 650°C for 30 min.) plasma sprayed HA coatings exhibited different morphological changes after immersion in SBF for different periods of time. It has been reported that due dissolution of the coatings multiple cracks appeared on as-received coatings after three hours soaking. These micro-cracks and pores resulted from dissolution acts as nucleation sites for the nuclei to anchor. As the immersion time increases the original morphology of as-received coatings changed completely. Conversely, neither surface dissolution nor precipitation was observed in case of heat treated coatings even after 7 days of immersion. The similar results are assessed by Lee et al. (2005) and Fernandez et al. (2007). This is owing to the fact that the amorphous phase in the as-received coating recrystallize into superfine crystallites without altering the coating morphology. This showed that the heat treated coatings were more stable in physiological solutions compared to as-received coatings.

In vitro behavior of plasma sprayed HA35 wt% YSZ15wt%/ Ti-6Al-4V50wt% biocomposite coatings were investigated by Gu et al. (2004) after immersion in SBF. It has been shown that many secondary phases such as amorphous calcium phosphate, α-TCP and CaO were present before immersion in SBF. After 1 week of immersion, α-TCP phase disappears completely whereas CaO phase disappears after 4-weeks of immersion. This shows that all the secondary phases are dissolved after 4-weeks immersion. Morphological changes showed that the coating immersed in SBF, micro-cracks were exposed on the coating surface due to dissolution after 1 day of immersion. As the immersion time increases, the crack density and crack size increases which is attributed to dissolution in SBF. These morphological changes are nearly similar as investigated by Gu et al. (2003).

The in-vitro behavior of atmospheric plasma sprayed pure HA and HA/Ti composite coatings were reported by Zheng et al. (2000) after 2-weeks immersion in SBF. It has been revealed that the secondary phases such as TCP and CaO disappear completely after 2-weeks of immersion which is attributed to the reaction of TCP and CaO with water and their dissolution in water. After immersion in SBF the surface of pure HA, HA/Ti 20 wt% and HA/Ti 60 wt% composite coatings were completely covered by carbonate containing apatite layer which confirm the good bioactivity of the coatings. These results are correlated with the results found by Zheng and Ding (2000).

Mechanism of precipitation of the precipitated bone like apatite layer on HVOF sprayed calcium phosphate coating was investigated by Khor et al. (2003) and Lima et al. (2007) after in-vitro incubation in SBF. It has been observed that the precipitation of apatite was almost certainly a partially diffusion controlled process and it was also reported that the precipitation originally occurred at the place where dissolution took place. As the incubation time increases, the thickness of the precipitated apatite layer increases. The comparable results are also elicited by Haman et al. (1995) after immersion in Hank’s balanced salt solution (HBSS).

Ha et al. (1998) studied the changes in morphology of VPS sprayed HA coating after ageing in SBF and fetal calf serum (FCS) physiological solutions. Significant change in morphology was observed even after soaking for one day in SBF whereas in FCS no significant morphological changes were observed even after 28 days of immersion. This shows that the morphology of the VPS-HA coatings did not change significantly after immersion in FCS in contrast to immersion in SBF.

3 Mechanical Performance

3.1 Bond Strength

The bond strength degradation was reported by Chang et al. (1997) after immersion in SBF for pure HA and ZrO\textsubscript{2}/HA composite coatings. As shown in Fig 1, the percentage degradation of bond strength reached its maximum values for all the coatings after immersion.
5 days of immersion and a little improved after 10 to 20 days of immersion. The initial decay in bond strength was attributed to the dissolution of the coatings which reduces the cohesive strength of the coatings. The results also indicated that pure HA coating revealed more bonding decay after immersion compared to composite coatings. The improvement in bond strength after 10 days of immersion was as a result of the penetration of glue into the cavities formed in coatings due to dissolution, which falsely strengthens the coatings.

About 61% and 75% decrease in bond strength was observed by Fernandez et al. (2007) after 1 and 7 days of immersion respectively compared to as-sprayed coatings. A change in failure type was also observed which was adhesive-cohesive in nature before immersion, while a completely adhesive failure was found after immersion. In contrast to this no deterioration of bond strength was observed even after 7 days of immersion for heat treated coatings. This is attributed to the lack of degradation in SBF, but show a low level of biomimetic activity to form secondary apatite on the surface in contact with SBF.

Yang et al. (1997) investigated the in-vitro and in-vivo behavior of two types of HA coatings with relatively different microstructures, concentrations of impurity phases and indices of crystallinity. After 4-weeks immersion in SBF, approximately 32% bonding strength degradation was reported. This degradation in bonding was attributed to the weakening of interlamellar microstructure due to chemical dissolution of secondary phases in SBF.

It has been reported by Gu et al. (2003) that the bond strength of the coating degrades after ageing in SBF through chemical dissolution. After one week soaking, the bond strength decreases about 15.8% and upto second week soaking duration, it is evident that the coating shows a continuous degradation with a total of 31.6% reduction in original strength. This reduction in bond strength was attributed to the chemical dissolution of the coatings, which weakens the bonding of the lamella in the coating and the bonding of the interface between coating and substrate. The decrease in the bonding strength for the composite coatings is significantly lower as compared to pure HA coatings because they dissolve slowly in aqueous environments.

Gu et al. (2004) evaluated the effect of SBF on tensile bond strength of pure-HA and composite coatings. The results (Fig. 5) showed that the decrease in tensile bond strength for pure-HA coating was found to be about 78.1% whereas 35.2% and 27.7% reduction was observed for HA/Ti-6Al-4V and HA/YSZ/Ti-6Al-4V composite coatings respectively over the same period of immersion. It is evident that there is a drastic drop in tensile bond strength of pure-HA coating after immersion because of higher chemical dissolution in SBF in contrast to composite coatings. This dissolution causes higher bonding decay of HA coating at the interface of coating and substrate which resulted into drop of tensile bond strength.

### 3.2 Microhardness

![Figure 2 Percentage degradation of mechanical properties after immersion in SBF for 1, 2 and 4 weeks period [Gu et al. (2003)]](image)
It has stated by Gu et al. (2003) that microhardness decreases about 10.1% as shown in Fig. 2 after soaking in SBF for 1 week. This decrease in microhardness increases as the time duration of immersion increases. After second week it shows 17.1% decrease from the original value without soaking. This is due to the dissolution of the coating in SBF and it causes the depletion of the calcium phosphate layer during soaking. The indentation force during testing therefore is not resisted by the weakened structure of the coating after ageing in SBF.

Kweh et al. (2002) investigated the mechanical behavior of plasma sprayed spheroidized HA (SHA) coatings after ageing in SBF. Fig 3 and 4 showed the decrease in mechanical properties of as-sprayed and heat treated coatings after prolonged immersion in SBF. The declining trend was observed in microhardness as the immersion periods were increased. It was decreased about 7.1% after 2 weeks immersion for as-sprayed coatings as shown in Fig 3, which decreases to about 23.8% and 36.7% after 6 and 10 weeks of immersion respectively. This deterioration in microhardness was attributed to the depletion of calcium phosphate layer through the vigorous dissolution of the layer. It is evident from this drastic dip in microhardness that the as-sprayed coatings are having poor physiostability after 10 weeks of immersion. But in case of heat treated coatings (Fig 4), the dip in microhardness was much controlled and less drastic in comparison to as-sprayed coatings. This shows that the heat treated coatings possess superior physiostability and are less prone to biological demineralization.

Gu et al. (2004) investigated that the percentage decrease as shown in Fig 5 in knoop hardness is maximum for pure-HA coating compared to other two composite coatings. This is attributed to higher rate of dissolution of pure-HA coating in SBF. This dissolution weakens the interlamellar microstructure of coating which resulted into less resistance offered by pure-HA coating than composite coatings to indenter force after immersion in SBF for 8-weeks period.

### 3.3 Young’s Modulus

Gu et al. (2003) observed that during initial soaking period of 1 & 2 weeks, Young’s modulus decreases to about 12.2% and 18.4% respectively as shown in Fig. 2. This is attributed to the higher dissolution rate of the coating in SBF, but slowly the decrease in Young’s modulus starts to diminish after about 8 weeks of immersion due to the gradual decrease in dissolution rate and the continuous precipitation.

The effects of prolonged immersion in SBF on Young’s modulus of as-sprayed & heat treated coatings are shown in Fig 3 and 4 respectively. It is observed by Kweh et al. (2002) that Young’s modulus of the as-sprayed as well as heat treated coatings decreases as the immersion periods increased. After 2, 6 and 10 weeks of ageing, the Young’s modulus dropped about 3.5%, 16.4% and 37.5% respectively in case of as-sprayed coatings. In contrast to this, the heat treated coatings, a corresponding drop in Young’s modulus of about 22.8% was noted, indicating heat treated coatings are more stable in SBF than as-sprayed coatings.
It is evident from Fig 5 that pure-HA coating has minimum percentage decrease in young’s modulus than composite coatings. This is attributed to the brittle nature of HA which resulted into the little change in elastic recovery of pure-HA coating before and after immersion in SBF. In contrast the composite coatings exhibit significant decrease in elastic recovery after immersion compared to before immersion in SBF as reported by Gu et al. (2004).

The young’s modulus of the bone like apatite layer precipitated on HVOF sprayed calcium phosphate coating was evaluated by Khor et al. (2003) after soaking in SBF for 42 days. The elastic modulus of the apatite layer formed at earlier stage (< 1 weeks incubation period) was relatively higher than that formed during later stages. This was attributed to dense precipitates formed at the coating and apatite layer interface. The elastic modulus of apatite layer exhibited a value of approximately 120 GPa obtained from nano-indentation.

3.4 Wear Behaviour in SBF

Sathish et al. (2011) studied the wear behavior of nano-ceramic coatings in SBF deposited on Ti-13Nb-13Zr alloy by atmospheric plasma spray technique. The sliding wear test of nano structured coatings (Al2O3-13TiO2, ZrO2 and bilayered ZrO2/Al2O3-13TiO2) was carried out in Hank’s solution maintained at 37°C for 105 cycles using reciprocatory wear tester. It has been observed that bilayered coating exhibited the highest wear resistance around two hundred to five hundred fold increase in the wear resistances when compared with that of the nano structured Al2O3-13TiO2 and ZrO2 coatings. The ZrO2 offered least resistance to wear among the three coatings and this is due to the cracks that have been generated during plasma spraying of coatings. The high wear resistance of bilayered is due to the higher adhesion, hardness and less porosity of the coating.

Balani et al. (2007) has conducted the pin-on-disc wear test on bare substrate, plasma sprayed HA coating and carbon nanotube (CNT) reinforced HA coating in SBF environment. The zirconia (ZrO2) pin was used to slide against the coatings and bare substrate. Higher wear resistance was observed for HA-CNT coatings when compared to pure HA coating and that of bare substrate. The reduced wear rate of HA-CNT coating is attributed to CNT reinforcements which act as bridges to connect splats and restrict the separation of adjacent splats.

4 Summary

Following may be summarized from the previous work:

1. The dissolution rate of pure HA coating is more as compared to composite coatings.
2. It is observed from the morphology of heat treated coatings that they are less susceptible to dissolution as compared to as-sprayed coatings.
3. The quantity and size of the precipitation increases as the immersion time of coatings increases.
4. The surface roughness of the coatings increases due to surface dissolution of the coatings after immersion in SBF.
5. The dissolution of the amorphous phases is evident from the rapid increase in calcium ion concentration in SBF solution.
6. The apatite layer formation after immersion on the coating surface indicates a good bioactivity of the coating.
7. The as-sprayed coatings showed that the mechanical properties decrease after immersion in SBF. Whereas, also heat treated coatings exhibited the similar deteriorating trend in mechanical behaviour but shows less drop compared to as-sprayed coatings (Fig 3 and 4) and are more stable in SBF.
8. Reinforced HA coatings are more wear resistant in physiological solutions than pure HA coatings and bare substrates.

References


