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# **Comparison between the SBF response of hydroxyapatite coatings deposited using both a plasma-spray and a novel co-incident micro-blasting technique**

J.N.Barry, D.P.Dowling

School of Mechanical and Materials Engineering, University College Dublin, Belfield, Dublin 4, Ireland.

james.barry@ucdconnect.ie , denis.dowling@ucd.ie

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## **Abstract**

This paper reports on the response of hydroxyapatite (HA) coatings, fabricated using two deposition technologies, to immersion in simulated body fluid (SBF). The deposition methods used were: plasma spray, a commercial standard, and CoBlast, a novel low temperature microblast technique. In the case of the latter, HA coatings are deposited by simultaneous blasting HA and abrasive powders concentrically at a metallic substrate, resulting in a thin layer of HA (approx. 2.5  $\mu\text{m}$  thick). Groups of the CoBlast and plasma spray HA coatings were immersed in 7 ml of SBF solution for 1, 2, 4, 7, 14 and 28 days, and were subsequently removed and examined for any alterations caused by the SBF solution. It was noted from this study that the CoBlast HA coatings appeared to undergo a two step calcium phosphate recrystallisation process; initial homogenous nucleation and subsequent heterogeneous nucleation. Conversely recrystallisation on the plasma spray coatings appeared to proceed largely through a heterogeneous nucleation process. Two factors that may influence the differences in HA recrystallisation is the presence of amorphous HA resulting in rapid dissolution, and/or the significantly lower surface area (roughness) offered to the SBF solution by the CoBlast coatings. The interpretation of recrystallisation mechanisms from this preliminary study is limited however by the differences in coating morphology and thickness (27 versus 2  $\mu\text{m}$ ) for the plasma spray and CoBlast HA coatings respectively.

# 1. Introduction

The bioceramic, hydroxyapatite (HA), is widely used in medical device applications such as dentistry, orthopaedics and maxillofacial reconstructions to enhance cell attachment to the device surface [1-4]. HA's success is due to its similarity in composition with the inorganic phase of human bone and teeth [3, 5]. In orthopaedics, this similarity provokes a natural response from the body as if the HA material were bone, where the Osteoblast and Osteoclast cellular action is unaffected [5]. However despite the biological benefits of using HA, in its bulk form, it is a brittle material and has both low tensile strength and impact resistance [3, 5]. As a consequence, in orthopaedic and dentistry, HA is more often used as a coating on metallic implants (cement-less) to enhance their biological response, while the metal component provides the durability and functionality [5-7]. There exist several processing paths for the deposition of HA coatings, such as; sol-gel, ion-beam, electrophoretic, high-velocity oxy-fuel spray (HVOF) and plasma spray [3]. The plasma spray process however is most often employed for commercial HA coatings on orthopaedic and dental implants [3-5].

A significant issue with the plasma sprayed HA coatings is the thermal modification of the HA powder's crystalline phases during the deposition process, resulting in multi-phase coatings. That is, plasma spray HA coatings do not only consist of crystalline HA but phases such as amorphous HA, beta-tricalcium phosphate ( $\beta$ -TCP), alpha-tricalcium phosphate ( $\alpha$ -TCP, results from  $\beta$ -TCP above 1600 K) and tetra-calcium phosphate (TTCP) [3, 5, 8]. Hench and Wilson have reported that some change in the crystalline phases of HA may be beneficial for early cell response [5]. Long term implant studies however have shown the presence of these phases could increase the solubility of the HA coatings, which in turn may result in device loosening [9, 10]. This study reports on a novel low-temperature deposition process called CoBlast™. In this process both HA and abrasive (MCD) powder jets impinged simultaneously at a concentric point on a metallic surface, resulting in a HA coating. One particular advantage of the CoBlast™ process is the depositions occur at close to room temperature, thus helping to avoid the phase changes seen in the plasma spray process [11]. This should result in a HA coatings with lower solubility levels [5].

In discussing HA coatings and their deposition processes, the most critical factor to be considered is the *in vivo* response and performance of the respective coatings. Simulated body fluid (SBF) solutions have been widely used to mimic the *in vivo* surface response of bioactive ceramics to body fluids [12-14]. This is achieved by the close similarities in pH and ion concentration to human blood plasma, where the initial dissolution and subsequent recrystallisation seen *in vivo* is replicated *in vitro*. The focus of this study is to evaluate the response of CoBlast deposited HA coatings to immersion in an SBF solution at 37°C. Plasma spray HA coatings are utilised for benchmarking and

comparison purposes, as the response of plasma spray HA coatings to immersion in SBF solutions have been well documented [7, 15].

## 2. Experimental details

### **CoBlast™ HA coating depositions.**

The CoBlast HA coatings were deposited using HA powder purchased from S.A.I. (Science Applications Industries, France), with a mean particle size of 37  $\mu\text{m}$ . The depositions were performed with the abrasive apatite powder called MCD (Himed, USA). Titanium alloy (grade 5, Ti6-Al-4V) test substrates, with dimensions 20×20×1 mm, were obtained from Lisnabrin Engineering Ltd (Ireland). The test substrates were polished to 1200 grit with silicon carbide paper and ultrasonically cleaned consecutively with methanol and acetone solutions for 5 minutes to remove any residual particles from the polishing process. The CoBlast™ depositions were then performed on the prepared substrates. Subsequent to the deposition experiments the HA coated samples were ultrasonically cleaned in deionised water to remove any particles on the surface of the coating.

### **Plasma HA coating depositions.**

The approx 27  $\mu\text{m}$  thick plasma spray coatings were deposited by APS Materials Inc. (Ireland), with the same HA powder and test substrates as used for the CoBlast™ study. Prior to depositing the coatings the substrates were grit-blasted to aid adhesion of the plasma spray coating to the metallic surface. This grit-blast procedure is routinely performed with commercial coatings [5]. The plasma spray coatings were deposited using an atmospheric plasma spray system, under the typical processing conditions used for commercially deposited HA coatings. As for the CoBlast samples, prior to testing the samples were ultrasonically cleaned in deionised water to remove any residual particles present on the surface of the coating.

**Immersion of coatings in SBF solution.** The SBF solution was prepared by dissolving the following reagents into distilled water; NaCl, NaHCO<sub>3</sub>, KCl, K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O, MgCl<sub>2</sub>·6H<sub>2</sub>O, CaCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub>, (CH<sub>2</sub>OH)<sub>3</sub>CNH<sub>2</sub> and using 1kmol/m<sup>3</sup> HCl to adjust the ph to 7.25 [12]. The solution is designed to closely match the ion concentration within human blood plasma, as detailed in table 1.

Table 1: A comparison of ion concentration [mmol/l] within human blood plasma and simulated body fluid (SBF) [12]

	Ca <sup>2+</sup>	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	HPO <sub>4</sub> <sup>2-</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	SO <sub>4</sub> <sup>2-</sup>
Human Blood Plasma	2.5	103.0	27.0	1.0	5.0	1.5	142.0	0.5
Simulated Body Fluid (SBF)	2.5	147.8	4.2	1.0	5.0	1.5	142.0	0.5

The HA coated samples were placed in sterile 6-well cell culture plates and immersed in 7 ml of SBF solution. The multi-well plates, with samples and SBF, were then sealed to retain their sterility and placed in an incubator at 37°C. The coated samples were removed from the SBF solution for testing after immersion times of 1, 2, 4, 7, 14 and 28 days. The removed samples were gently immersed three times in de-ionised water to remove any residual SBF solution. The samples were allowed to dry at room temperature and were subsequently placed in an oven at 50°C for 1.5 hours prior to testing.

### **Coating characterisation.**

A Scanning Electron Microscopy (SEM, TM-1000 Hitachi high-technologies) operating in back-scatter mode was utilized to image the coatings. Data was taken at a magnification of x2000 over 5 random points on each coating. This technique was primarily used to assess the morphological response of the coatings to immersion in the SBF solution.

The roughness of the HA coatings were measured using a WYKO NT1100 optical profilometer, operating in vertical scanning interferometry (VSI) mode. Measurements were taken at a magnitude of  $\times 25.0$ , over 10 random areas (area dimensions:  $247 \times 187 \mu\text{m}$ ) on each sample, where the roughness parameters  $R_a$  (arithmetic average) and  $R_t$  (height of the profile) were obtained.

An EDX (Swift-ED, Oxford Instruments Analytical) module attached to the Hitachi SEM was utilised for elemental analysis of the coating, operating with a raster scan pattern. The same points as imaged using the SEM were assessed using the EDX module. The Ca/P ratio within the HA coatings, was used to highlight any modification of the precursor HA powder during deposition and also of the coated surface upon exposure to SBF solution. Pressed tablets of the HA precursor powder were evaluated as a reference to assess any deviations from the precursor powder.

X-Ray Diffraction (XRD) was carried out using a Siemens D500, to assess the crystalline structure present in the CoBlast™ and plasma spray coatings before and after immersion. Three random points were analysed per sample, on 2 samples of each coating, over the detector range of 25° to 40° with a resolution of 0.02° and a grab time of 3 seconds.

## **3. Results**

**Coating Morphology.** Figure 1 displays the typical surface morphologies observed at the immersion times of 0 (or Pre-SBF), 7 and 28 days for the plasma spray and CoBlast coatings. Subsequent to SBF immersion, the plasma spray surface morphology was found to be significantly altered, even after immersion for 1 day. Small spherical deposits were observed on the HA coating surface. The formation of these spheres would suggest that the main mechanism of recrystallisation is heterogeneous nucleation, and the subsequent expansion of these spheres after longer immersion

times supported this conclusion. Weng et. al. attributes the formation of these nucleation sites to the rapid dissolution of the amorphous HA present in the plasma spray coatings, thus causing a significant ion imbalance in the SBF solution [15]. It was also noted the cracks observed in Pre-SBF samples were still visible even after 28 days immersion. The response observed to SBF immersion in this study is typical of that which has previously been reported for plasma spray coatings [7, 15].

Unlike the plasma spray deposited HA coatings, the CoBlast coatings were found to remain largely unchanged compared to their pre-SBF morphologies up to a period of 7 days immersion. The spherical deposits seen on plasma spray coatings were found only on small areas of CoBlast coatings at this time point. The formation of these spherical deposits would suggest the beginning of heterogeneous nucleation, and the relatively small amount that was present on the CoBlast coatings up to 7 days immersion, may suggest that the mechanism of recrystallisation is homogenous nucleation up to this point. The delay in the formation of these spheres could suggest lower dissolution rates due to the high level of crystalline HA in the CoBlast coatings [15]. Another factor influencing these results however is a very significant difference in surface area offered to the SBF solution by the two coatings, due to the difference in thickness and roughness (Table 2). The significant reduction in spherical deposits could therefore be attributed to the lower surface area of the CoBlast coatings. In order to conclusively compare the mechanism for recrystallisation, trials would have to be carried out with coatings with similar thickness and roughness. The samples obtained for the 14 and 28 days immersion, showed signs of rounding on the angular or 'cliff-like' features present on the Pre-SBF CoBlast coatings, which would indicate heterogeneous nucleation. At 28 days immersion, the appearance of the CoBlast coating's morphology was much more rounded when compared with their Pre-SBF morphologies.

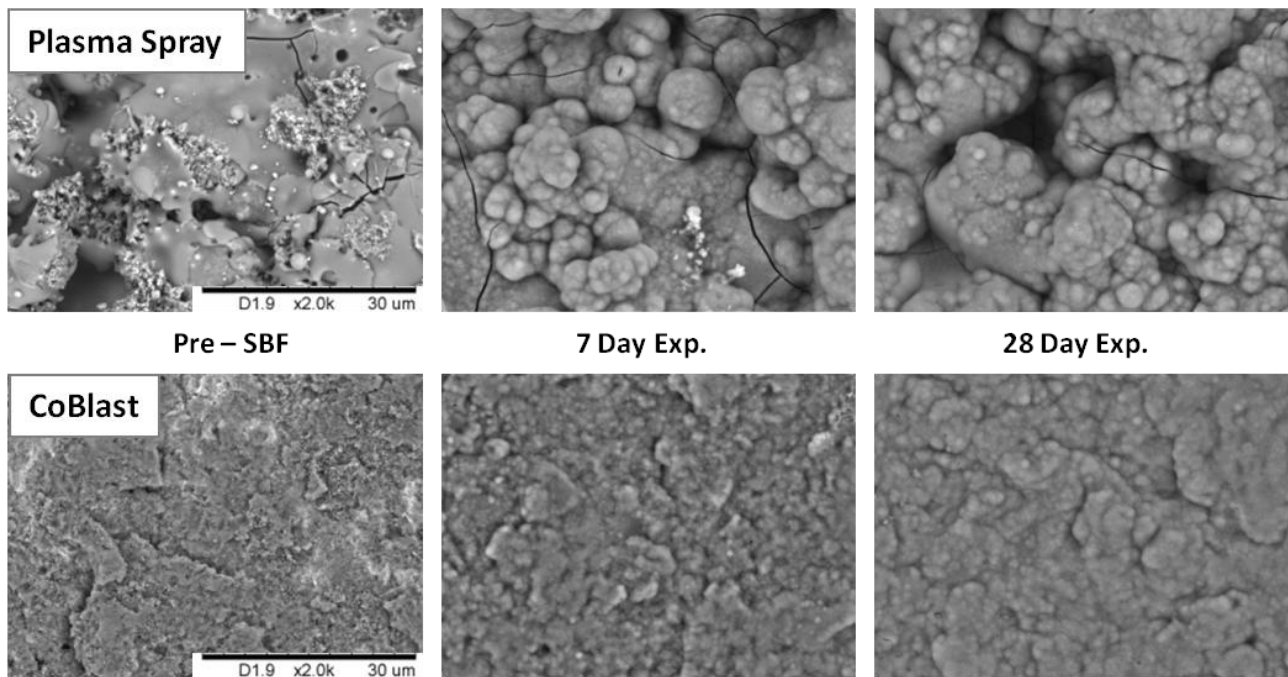


Figure 1: SEM surface morphologies images of the plasma spray and CoBlast coating at 0 (or Pre-SBF), 7 and 28 days immersion (all at magnitude  $\times 2000$ )

Table 2 shows the roughness results for the plasma spray and CoBlast coatings over the period of immersion. The results show that the immersion of the plasma spray coatings had a significant effect on the  $R_a$  and  $R_t$  values. This agrees with the SEM images showing a significant change in morphology even after only 1 day immersion. Conversely the  $R_a$  and  $R_t$  values of the CoBlast coatings were found to stay within the range of values obtain Pre-SBF. This would marry well with the SEM morphology images indicating no significant changes in morphology for the first 7 days immersion. Subsequent to this, the 14 and 28 days samples both displayed a drop in  $R_a$ . This drop in roughness coincides with the increased recrystallisation observed in the SEM images.

Table 2: Roughness data for the plasma spray and CoBlast coatings after SBF immersion.

		Pre-SBF	1 Day	2 Days	4 Days	7 Days	14 Days	28 Days
Plasma spray	$R_a$	5.55 $\pm$ 1.01	6.83 $\pm$ 0.65	6.74 $\pm$ 0.89	7.16 $\pm$ 0.96	6.46 $\pm$ 1.12	6.77 $\pm$ 0.8	6.72 $\pm$ 0.8
	$R_t$	42.23 $\pm$ 7.46	69.37 $\pm$ 8.97	66.47 $\pm$ 8.37	66.28 $\pm$ 8.01	67.12 $\pm$ 8.63	65.00 $\pm$ 9.21	71.33 $\pm$ 11.01
CoBlast (MCD)	$R_a$	1.11 $\pm$ 0.21	1.35 $\pm$ 0.12	1.34 $\pm$ 0.1	1.30 $\pm$ 0.06	1.30 $\pm$ 0.11	1.26 $\pm$ 0.07	1.16 $\pm$ 0.08
	$R_t$	24.82 $\pm$ 4.76	30.44 $\pm$ 4.31	38.86 $\pm$ 6.08	30.40 $\pm$ 8.05	32.48 $\pm$ 4.26	30.33 $\pm$ 5.86	30.36 $\pm$ 5.48

**Coating composition and crystallinity.** Figure 2A gives the elemental results obtained from the EDX analysis of the CoBlast coatings and shows relative changes after the immersion times shown. The approx. 2.5  $\mu\text{m}$  thickness of the CoBlast coatings means that at the EDX system (operating at

15kV) penetrated the HA layer resulting in the detection of substrate elements (note the Pre-SBF result in figure 2A). This figure also shows that with increasing immersion time the level of substrate elements detected decreases, indicating an effective increase in thickness of the CoBlast HA coatings. This would indicate that homogeneous nucleation is occurring at this stage of immersion, as a layer grows over the HA coating increasing its thickness. The plateau in substrate elements detected between 14 to 28 days immersion would suggest little coating growth occurred in this time. This would agree with the previous finding, where after 7 days immersion the driving force for recrystallisation becomes heterogeneous nucleation resulting in no significant coating growth but smoother surface morphology. The XRD scans carried out on the CoBlast HA coatings, reflected this increase in coating thickness with an increase in the peak intensity after longer immersion times.

Figure 2B displays the Ca/P ratio response of the plasma spray coatings with SBF immersion time. The dotted line represents the Ca/P ratio obtained for the precursor HA powder. Upon immersion in the SBF solution a significant drop in the Ca/P ratio is observed in the plasma spray coatings, this may be associated with the rapid dissolution of the amorphous HA phase which predominantly consists of calcium [7, 15]. Following this initial drop, a trend of increasing Ca/P ratio back to the original value of 3.2 is seen, and then this appears to plateau between 14 and 28 days immersion. This trend can be explained by considering the SBF solution to be a metastable 'closed loop' solution (supersaturated in calcium and phosphorus ions), therefore any dissolution of calcium away from the coating requires subsequent recrystallisation of calcium onto the coating surface for a chemical balance to remain. This result is supported by the findings obtained by Weng et. al. who observed an initial increase in Ca ions in the SBF solution over the HA, followed by a reduction associated with recrystallisation [15]. XRD results showed the plasma spray HA coatings became more crystalline with immersion time indicating a loss of non crystalline HA phases [7, 15]. No change in Ca/P ratio was observed in the CoBlast HA coatings, with immersion in the SBF solution and the XRD data indicated no increase in crystallinity after 28 days immersion for these coatings.

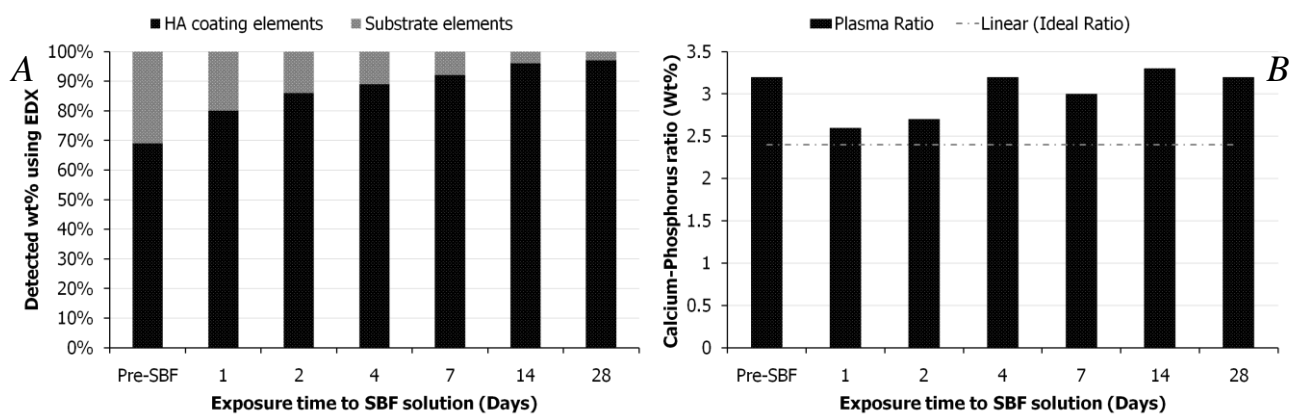


Figure 2, A: Influence of immersion time on the EDX detected elements on the CoBlast coatings, B: Ca/P ratio response of the plasma spray coatings to SBF immersion

## 4. Conclusions

*In-vitro* SBF solution (acellular) studies were used to investigate the potential *in vivo* response of both CoBlast and plasma spray deposited HA coatings. A study of HA coating crystallinity after immersion in SBF demonstrated that the CoBlast coatings were found to be largely unaffected even after 28 days immersion. In contrast the plasma spray coatings were found to become more crystalline with increasing immersion time, indicating dissolution of the non crystalline HA phases. This study validated the SBF solution test methodology as the changes observed have been reported previously for plasma spray coatings, where plasma spray coatings undergo a largely heterogeneous nucleation even after only one day immersion. The CoBlast coatings in contrast appeared to undergo two stages of recrystallisation, initially homogenous nucleation and subsequent to 7 days immersion, a heterogeneous nucleation mechanism. The initial stage appeared to allow a calcium-phosphate layer to grow on the CoBlast HA coatings without significantly altering its morphological appearance, resulting in an increase in the overall coating thickness and roughness. The next stage gave rise to a reduction in the roughness of the HA coatings, with little or no change in the coating thickness (based on EDX analysis). The difference in coating response could be attributed to two main factors, the presence of amorphous HA in the plasma spray HA coatings and/or the significantly lower surface area offered by the CoBlast coatings. These results however should only be considered as preliminary. In order to obtain more quantitative data on recrystallisation mechanisms, comparisons of coatings with similar thickness and morphology would be required. This would be difficult to achieve given the processing limitation of these two deposition technologies, the CoBlast technique being limited to depositing HA thickness of  $\approx 2.5 \mu\text{m}$  while typical plasma spray coatings thickness is  $\geq 27 \mu\text{m}$ .

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