

Phase Evolution in Nano Titania Doped Hydroxyapatite Coatings

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Introduction

Hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ or HAP has been widely used in dental and orthopedic implants, due to its chemical and crystallographic similarity with bone minerals. It has also been used to collect pollutants and selectively adsorb proteins in chromatography. The functionality of HAP can be enhanced further by doping it with titania. Importantly, the efficacy of titania lies in its size (micro/nano) and phase (rutile/anatase). For example, HAP does not decompose the absorbed material and saturates over a period losing the absorption capacity [1]. Having nanometer size titania in anatase phase, could induce photocatalytic activity and bacterial decomposition in HAP [1]. On the other hand, for osteointegration the rutile phase is preferred [2]. Therefore, obtaining the appropriate phase and particle size is of crucial importance in HAP and titania composite coatings. In this study we adopted a novel hybrid approach in which solid HAP powder and liquid titania precursors are injected to a plasma jet independently. Nano titania is synthesized in the flight and subsequently get embedded into the HAP matrix, resulting in a composite coating. The uniqueness in this approach lies in the synthesis of nano titania in flight [3] which circumvents the preparation of nanopowders, their collection and mixing with HAP to deposit a composite coating [1, 2]. Further, the independent injection of precursor materials facilitates the necessary thermal cycle needed for appropriate phase formation. Additionally, the composition can be tailored in-flight, resulting in a functionally graded coating which is difficult by premixed powders.

Experimental

A commercial high purity HAP powder (CAPTAL 60, Plasma Biototal Ltd, Derbyshire, UK) was used as the matrix material. The first liquid precursor (named “solution” or “S” hereafter) was prepared by dissolving titanium isopropoxide (97 wt.%, from Alfa Aesar, Ward Hill, MA, USA) in an ethanol solvent with 10 ml Acetic Acid and 5ml Hydrogen Peroxide to make a concentration of 0.00316M. The second precursor (named “powder suspension” or “PS” hereafter) was prepared by suspending preprocessed anatase titania (99.9 % Sigma Aldrich) in ethanol with triethyl phosphate as a dispersant at similar concentration. The liquid precursor was atomized and injected to the plasma jet after the injection point of the HAP powder. The DC plasma torch employed was 100HE Gun (Progressive Technologies, Grand Rapids, MI, USA). Coatings were sprayed on grit blasted and acetone cleaned titanium coupons. Substrate temperature was measured by a

K-type thermocouple placed on the front surface of the coupon. When desired, compressed air was used to cool the substrate from the back.

Results and Discussion

Prior to the synthesis of the composite coatings, parameters to achieve the desired phases in both the materials were investigated. The XRD patterns of HAP coatings sprayed using different conditions are shown in Fig. 1. The major HAP peaks were preserved in the coatings made at 45 KW power suggesting minimal physico-chemical changes in the HAP. However, at 98KW the emergence of β -TCP peak and the amorphous phase is quite apparent. It is to be noted that these phases are undesirable in the HAP coating.

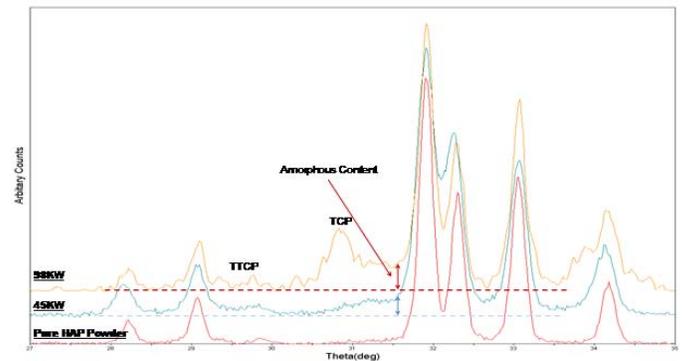


Figure 1: XRD patterns of the starting HAP powder as well as the coatings made at 45KW and 98 KW power.

Parametric investigation (45kW-98kW) on titania coatings was performed using the precursor, “PS”. With increasing power level, the fraction of anatase phase increased in the coating. At 65kW adherent coatings with significant anatase phase was possible. It was observed that anatase formation was favored by high quench rates, which is possible by heating to a higher temperature and then cooling rapidly. Fig. 2 presents the influence of substrate quenching on the phase evolution at 65kW. Without substrate cooling, the temperature reached 900°C and rutile phase dominated the coating although the starting material was entirely anatase. It is to be noted that conditions (high power, high quenching) that favored anatase formation, led to unwanted phases in the HAP. Therefore, a compromise was needed for the fabrication of the composite coatings which would enable HAP phase preservation while forming anatase phase. The gun power in the range of 65kW was found to be best for both the materials.

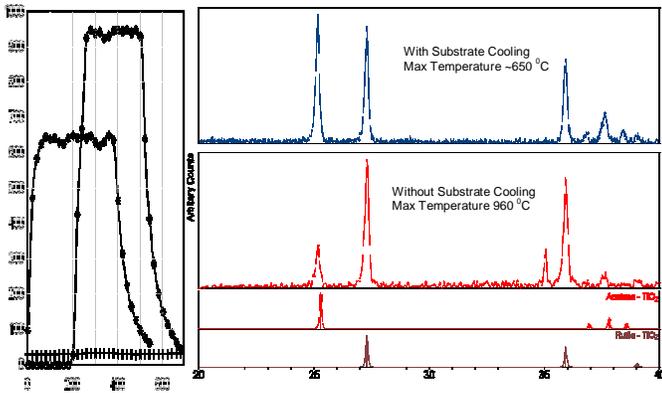


Figure 2: Influence of substrate cooling on the phase evolution of titania coatings made from precursor “PS”.

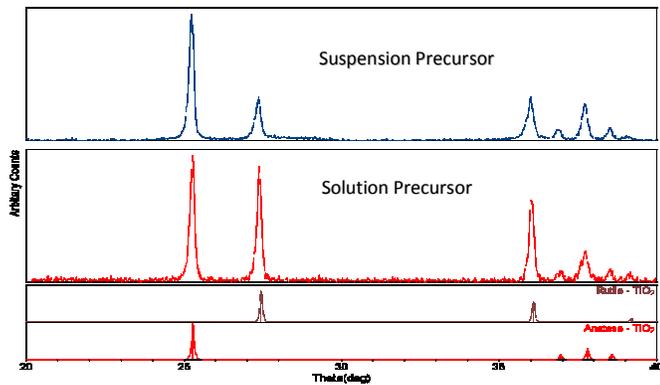


Figure 3: XRD patterns of titania coating made at 65 kW from precursors PS and S respectively.

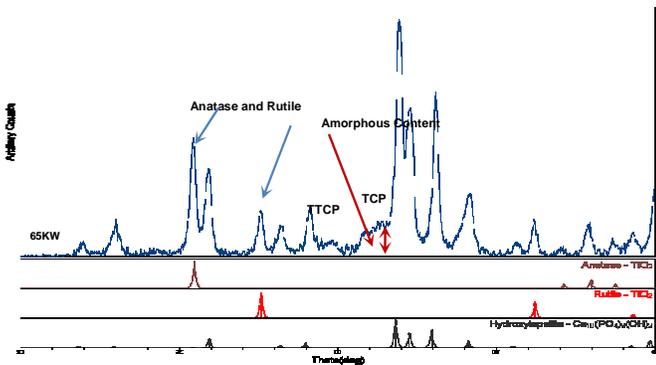


Figure 4: XRD of HAP + titania coatings at 65 kW from precursor “S”.

Fig. 3 shows the XRD of coatings made from precursor PS and S under identical conditions. Rutile phase was more dominant in the coating made from titanium isopropoxide solution precursor compared to that of the TiO_2 suspended precursor. The reason behind this is still under investigation. Fig. 4 presents the XRD of the composite coating containing

HAP and titania. As seen, both anatase and rutile phases are present. The undesirable β -TCP and amorphous contents are also small in this coating. Cross section analysis of the coatings, confirmed a uniform distribution of titania with different morphologies as shown in Figs. 5. In addition to ultrafine spherical particles, acicular shaped titania splats with high aspect ratio, were distributed across the thickness. Ye *et al.*, [1] have synthesized composite coatings by agglomerating nano titania and HAP powder together. Their coatings have demonstrated distinct photocatalytic effect despite the occurrence of the particles in large clusters. Therefore, we expect the current coatings to perform well even if acicular shaped titania splats are present in addition to the ultrafine particulates.

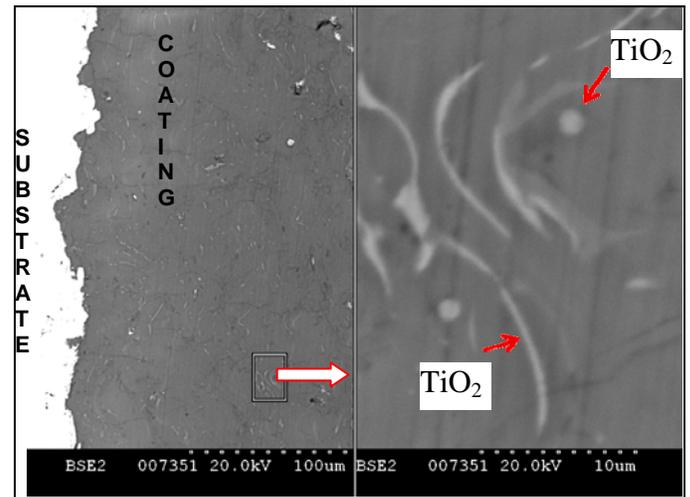


Figure 5: Cross sectional view of HAP + titania composite from precursor “S”.

Conclusions

Dense HAP coatings with well dispersed titania particulates were obtained by this new hybrid approach. Within a bound it was possible to vary the anatase to rutile ratio in the composite coatings while suppressing the emergence of undesirable amorphous and TCP phases.

References

1. Ye, F., Ohmori, A., Tsumura, T., Nakata, K. and Li, C. Microstructures and Compositions of Photocatalytic Plasma-Sprayed Titania-Hydroxyapatite Coatings. *J. Therm. Spray Technol.*, **16**(2007) 776-782.
2. Cannilloa, V., Lusvardhia, L. and Sola, A. Production and Characterization of Plasma-sprayed TiO_2 -Hydroxyapatite Functionally Graded Coatings. *J. Euro. Ceram. Soc.*, **28**(2008) 2161-69.
3. Chen, D., Jordan, E., Gell, M. and Maz, X. Dense TiO_2 Coating Using the Solution Precursor Plasma Spray Process. *J. Amer. Ceram. Soc.*, **91**(2008) 865-872.