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•CaP coating on PEEK Varies upon Processing Conditions •

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INTRODUCTION The predominant line of thought in the orthopedic community regarding plasma sprayed hydroxyapatite (HA) coatings stability is that these coatings rapidly dissolve. However, HA coatings have complex microstructures with phase, structure and chemical composition variations mainly determined by plasma spraying and starting material conditions. While HA-based and other CaP coating groups remain largely known as a single entity, some of process-induced changes may not be acceptable for biomedical applications. Also, 100% crystalline HA shows degradation rate orders of magnitude lower than other calcium phosphate (CaP) compounds such as tricalcium phosphate (TCP), tetracalcium phosphate (TTCP) or even amorphous HA [1]. This study examines the crystalline structure and dissolution of HA and other CaP plasma-sprayed coatings obtained from different plasma spraying conditions.

METHODS Polyetheretherketone (Invisio/Victrex's general grade PEEK, UK) samples were coated using atmospheric plasma spraying (APS) with : i) crystalline HA ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, Plasma Biotol, UK), ii) α TCP ($\text{Ca}_3(\text{PO}_4)_2$, *idem*) and iii) β TCP ($\text{Ca}_3(\text{PO}_4)_2$, *idem*). Coatings were produced using two different APS conditions in order to exacerbate crystalline content (CC) and phase variations (referred to "normal" and "hot"), as described in Table 1. These conditions were chosen to produce different CaP phases and/or structures offering different mechanical properties and dissolution kinetics.

Table 1. APS parameters for the HA and CaP coatings

Parameter	Normal	Hot
Plasma gas (slpm*)	Ar (60)	Ar (50) He (23.5)
Carrier gas (slpm*)	Ar (4)	Ar (4)
Current (A)	500	700
Voltage (V)	30	34.8
Power (kW)	15	24.4
Powder feed rate (rpm)	2	2 (1 for α TCP-hot)
Spray distance (in.)	4	4

* standard liters per minute

To study the coatings degradation kinetics the samples were incubated in DMEM solution (6 cm²/ml) subjected to 100 rpm and 37°C for 231 days, as per standard ISO/AAMI ceramic degradation guidelines [2]. After every 7 days, the condition media pH, samples net weight changes (following sample ddH₂O washing and vacuum oven drying at 60°C for 12 h), crystalline structure and content from X-ray diffraction (XRD) were recorded. Relative weight loss was taken with respect to initial weight normalized by non-coated sample baseline (PEEK).

RESULTS Characteristics of coatings: The coatings crystalline structure and content from XRD are summarized in Table 2. These results indicate that:

- 1) Although the dominant phase of APS HA remained HA, APS conditions modulated the crystalline content considerably, from a conventional 55% to very low 15% with respect to ISO standards [3] and the trace phases (TTCP and CaO) due to HA low stability at high temperatures.
- 2) For α TCP, normal APS conditions led to high CC (87%) while hot APS conditions led to lower CC (76%).
- 3) For all β TCP coating, β TCP transformed into α TCP due to its instability at APS temperatures (β TCP \rightarrow α TCP at 1180°C [4]).
- 4) β TCP-normal led to similar CC (83-86%) as α TCP-normal, while β TCP-hot resulted in important CC reduction compared to α TCP-hot in addition to CaO traces due to low stability at high temperatures.

Table 2. Crystalline structure and content of coatings

Coating	Dominant Phase	CC (%)	Traces (< 1%)
HA-normal	HA	55.2	TTCP
HA-hot	HA	15.3	CaO
α TCP-normal	α TCP	86.7	---
α TCP-hot	α TCP	76.1	---
β TCP-normal	α TCP	82.5	---
β TCP-hot	α TCP	45.4	CaO

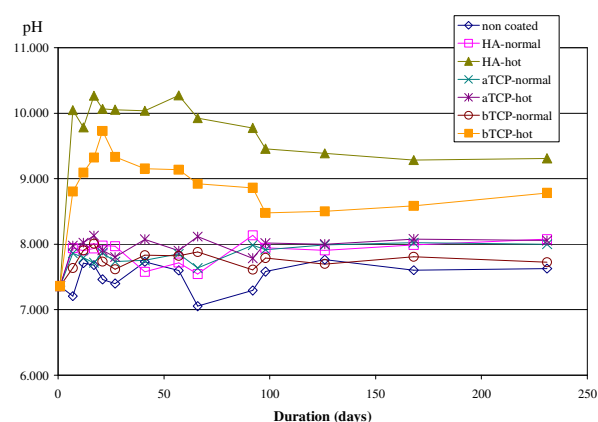


Fig. 1 pH variations vs. time for the coatings studied.

Coatings dissolution: No statistically significant weight loss was observed following 231 days of DMEM immersion under agitation (all were within $\pm 0.3\%$ relative weight). Figure 1 however shows that after only 7 days of DMEM incubation, the HA-hot and β TCP-hot coatings demonstrated a sharp pH increase to pH 10 and 9.5 respectively; with a near-linear decreasing pattern after day 7.

DISCUSSION Coatings with different crystalline phase and content were produced from those of feedstock HA, α TCP and β TCP, which were dependent on the APS conditions and not feedstock, as is predominantly assumed in the orthopedic community. Also, Crystalline content (CC) decreased for the highest temperature APS condition; trace phases were also affected by APS conditions; however CC alone cannot reflect coating quality and stability due to the existence of various HA structures and phases transformations. Despite that the coatings did not show significant weight losses after prolonged aggressive incubations; but significant rapid changes in pH were observed for HA-hot and β TCP-hot, indicative of a trend of higher dissolution with lower CC as expected for higher amorphous content. However different parameters show distinct degradation potentials as seen through the increased pH trends of the low CC coatings. The pH increase is not a degradation artifact but rather an OH⁻ ions release from the amorphous apatite, initiated by the temperature increase following the suggested reaction: Amorphous ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) \rightarrow (H_2O) ($\text{Ca}_5(\text{PO}_4)_3^+ + \text{OH}^-$

CONCLUSION When referring to HA and other CaP coatings, attention should be paid to describing the crystalline phase and their respective content, as plasma spraying conditions greatly affects the morphology and structure of the coatings. In particular, the resorption features of HA coatings cannot be generalized to a single behavior.

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ACKNOWLEDGEMENTS Financial support from Terray Corp. is gratefully acknowledged