



# *In vitro* evaluation of hydroxyapatite coatings with (002) crystallographic texture deposited by micro-plasma spraying



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## ABSTRACT

Hydroxyapatite (HA) coatings are usually deposited on the metallic implant to increase the biocompatibility and protect the bloodstream from harmful metal ions. Atmospheric plasma spray (APS) is known as a cost effective deposition method. However, the low crystallinity of APS deposited coating accelerates its dissolution in body fluid. We used micro-plasma spray (MPS) to develop chemically stable HA coatings, and performed APS as reference. Results showed that MPS deposited coatings exhibited (002) crystallographic texture while the reference sample did not. The texture intensity and crystallinity were improved by shortening stand-off distance. These suggested that different formation procedures of HA coatings were involved and three mechanisms were proposed by sketching typical splats. To evaluate the chemical stability of the coatings in a physiological environment, *in vitro* experiments were performed in Hanks' solution. Well crystallized (~100%) HA coating with the strongest crystallographic texture exhibited superior stability up to 14 days. Crystals with (002) orientation was more stable than that with (211) orientation. Hence columnar structure with nanopores emerged on the coating surface after incubation, and this may facilitate the future osteoblast growth. Furthermore, HA coating with weak and no crystallographic texture induced apatite layer. However, vertical cracks and cleavage at coating-apatite interface may cause coating separation.

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## 1. Introduction

HA is the main mineral composition for human bone and tooth [1]. HA coatings deposited on metallic implants can remarkably reduce the time for osseointegration [2], and prevent harmful metal ions diffusing into the bloodstream [3]. Due to the advantages of low cost and good mechanical properties of the deposited coatings, APS is a commonly used deposition manner [2], and has been approved by U.S. Food and Drug Administration (FDA). However, low crystallinity and phase purity are usually found in the APS deposited coatings [4]. The phases except well crystallized HA in the coating exhibit fast dissolution rate in a physiological environment [5], and the dissolution of those phases could accelerate the failure of plasma sprayed coating. Furthermore, excessive dissolution leads to rapid changes in ions microenvironment in body fluid and can be cytotoxic [6]. Thereby, for long-term and safe application, HA coating with high crystallinity and phase purity is pursued. MPS is an alternative plasma spray method using low plasma power ( $\leq 3$  kW). It is feasible to deposit coating on small-scale medical devices because of the concentrate plasma torch. Importantly, MPS can produce HA coatings with high crystallinity [7–11], and usually accompanied by

crystallographic texture at (002) [7–9,11]. Which is the preferential crystal orientation of natural HA in human tooth [1]. However, MPS deposited HA coatings are far from being fully understood. The influence of (002) crystallographic texture on *in vitro* behavior of HA coating is especially rarely studied.

In the present research, HA coatings were deposited by MPS and APS, respectively. The influence of spray parameters (plasma power, gas flow rate and stand-off distance) on phase composition and surface morphology of HA coatings were investigated. The formation mechanisms of HA coatings under various spraying conditions were discussed. Moreover, incubation experiments of representative HA coatings were analyzed to assess the chemical stability.

## 2. Materials and methods

Agglomerated spherical HA powder was employed as initial material with particle size of 45–63  $\mu\text{m}$  (Medicoat, Switzerland). Ti-6Al-4V disks ( $\Phi 15$  mm  $\times$  3 mm) substrate were sandblasted before deposition.

MPS (WPD-1, China) was used to fabricate HA coatings by using spray parameters listed in Table 1. Splats were also collected on sandblasted and polished substrates at stand-off distance (SOD) of 60 mm (MPS-I). Furthermore, APS (Sulzer Metco-9M, Switzerland) was employed to fabricate reference coating (Table 1).

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**Table 1**  
Parameters for MPS and APS in this work.

	APS	MPS-I	MPS-II
Voltage (V)	40	35	35
Current (A)	400	40	40
Working gas	Ar/H <sub>2</sub>	Ar	Ar
Gas flow rate (L/min)	30/0.4	1.2	1.2
SOD (mm)	110	60	110

The phase composition of coatings was measured by X-ray diffraction (XRD) using Cu K $\alpha$  incident radiation (Bruker/AXS-D8 Advance, Germany). The working voltage is 40 kV and current is 20 mA. Morphology observation was carried out on cold field emission scanning electron microscopy (SEM, SU8020, Japan) by secondary electron detector, with accelerating voltage of 1 kV. The Ca/P ratio was determined by energy dispersive spectrometer (EDS) with accelerating voltage of 20 kV.

*In vitro* experiments were performed in water bath container with shaking motion at 37 °C with Hanks' balanced salt solution (H8264, Sigma, USA). HA coatings were incubated for 6 h, 1, 3, 7 and 14 d to investigate the chemical stability in a physiological environment. And the splats were immersed for 3 h to study the dissolution behavior. Samples were weighted before and after incubation by analytical balance with precision of 0.01 mg (Sartorius-ME235S, Germany). The average weight of 3 samples was calculated.

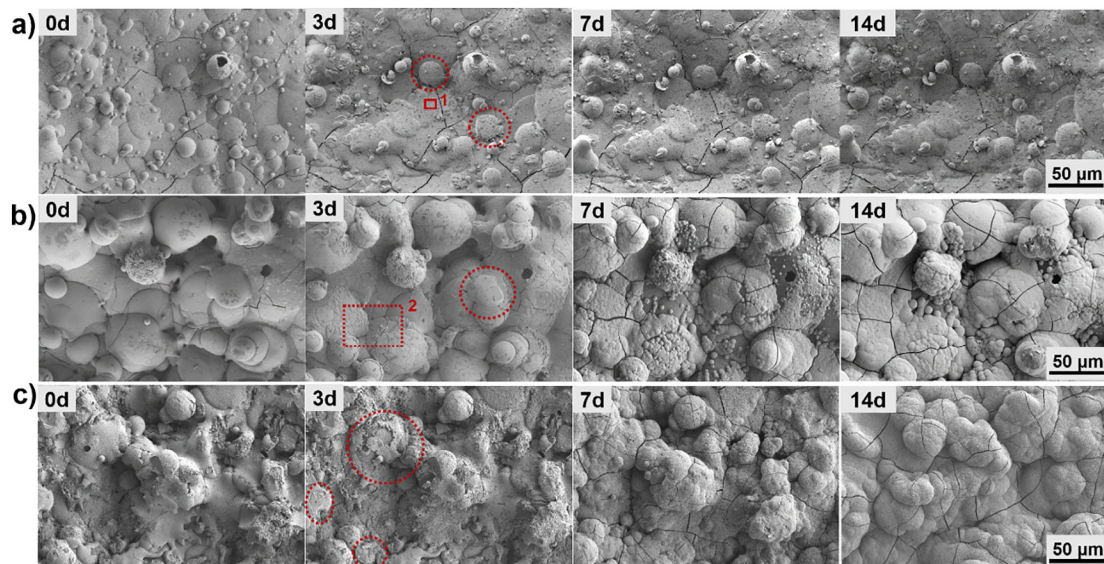
### 3. Results

Three representative coatings were mainly investigated, including the one deposited by MPS with SOD of 60 mm (MPS-I coating), 110 mm (MPS-II coating) and deposited by APS with SOD of 110 mm (APS coating). Fig. 1 shows the surface morphology changes of HA coatings with incubation duration. MPS-I coating exhibited well-flattened splats and small beads on the surface (Fig. 1a). MPS-II coating consisted of loosely adhering hemispherical splats (Fig. 1b). Craters with holes in the center were also observed. APS coating demonstrated many unmelted splats on the surface (Fig. 1c). These distinct characters of surface morphology indicate different formation mechanisms of HA coating under given conditions. During incubation, MPS-I coating showed minor changes in surface morphology and no apatite was precipitated up to 14 d (Fig. 1a). This suggests the outstanding stability of MPS-I coating in a physiological solution. Carefully observation revealed that several splat rims were dissolved after 3 d (circles, Fig. 1a). Meanwhile,

a typical embossment pattern emerged from coating surface (position 1, Fig. 1a), as illustrated in Fig. 2a. The embossment pattern contained mosaic-like particles with 200–500 nm in diameter and nanopores, implying the existence of columnar structured crystalline in MPS-I coating. MPS-II coating dissolved not only at splat rims (circle, Fig. 1b) but also on the splat surface after 3 d (position 2, Fig. 1b). The magnified microstructure of position 2 revealed that needle-like apatite (Fig. 2c) was preferentially precipitated at splat surface where dissolution has occurred (Fig. 2b). Apatite layer covered most areas of MPS-II coating after 7 d (Fig. 1b). However, gaps still existed after 14 d because that some apatite showed spherical shape, which distributed on the smooth areas where no dissolution has occurred (Fig. 1b). This phenomenon implies that the geometry of precipitated apatite depended on the surface morphology of coating, and was influenced by phase composition. APS coating dissolved severely after incubating for 3 d (circles, Fig. 1c). Apatite layer fully covered the observation area after 7 d (Fig. 1c), meaning that the precipitation rate of apatite is higher for APS coating than that for MPS-II coating. In addition, interconnected cracks were observed on the precipitated layer after 7 d for both MPS-II and APS coatings (Fig. 1b and c).

Cross section image shows that columnar grains were distributed on the top region of MPS-I coating along deposition direction (Fig. 3a). They were generally 200–400 nm in width and 2–10  $\mu$ m in height [11]. The Ca/P within columnar crystals was 1.54–1.61 (Fig. 3d), and it is near to the stoichiometric molar ratio of crystalline HA (1.67). Clear interface between precipitated apatite layer and coating was found on the MPS-II and APS coatings (Fig. 3b and c). Vertical cleavages were also observed within precipitated apatite layer. Both interface delamination and vertical cleavage became severer at thicker apatite layer on APS coating (~10  $\mu$ m) than that on MPS-II coating (~5  $\mu$ m). This indicates the risk of peeling off and fragmentation of thick precipitated apatite on coating. Compared to MPS-I coating, MPS-II coating and APS coating showed lower Ca/P of 1.36–1.48 near coating surface (Fig. 3d). This Ca-deficiency indicated the existence of amorphous calcium phosphate (ACP) and/or tricalcium phosphate (TCP) at the top region of coatings [12]. Furthermore, the precipitated apatite exhibited even lower Ca/P of ~1.2 on MPS-II coating (Fig. 3d). Whereas, it gradually increased from ~1.4 to ~1.67 with incubation on APS coating (Fig. 3d), indicating the phase composition changed within precipitated apatite.

Weight increase of HA coating after incubation of 14 d was following this rank: MPS-I coating < MPS-II coating < APS coating (Fig. 4). MPS-I coating demonstrated a slight weight loss after 3 d without further changes, confirming the chemical stability of MPS-I coating in Hanks'



**Fig. 1.** Surface morphology changes of a) MPS-I coating, b) MPS-II coating and c) APS coating with incubation time of 0 day, 3 days, 7 days and 14 days.

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