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Cold spray of agglomerated submicronic hydroxyapatite powders for biomedical applications

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Hydroxyapatite (HA) ceramic coatings are used for orthopaedic implants to favour bone growth. The main conventional process is plasma spray of pure HA powder. A solid state deposition process like cold spray of HA powder might have a great potential to achieve fully crystalline HA coatings. Moreover, HA by cold spray could also be envisaged favourably in case of thermosensitive polymeric biomaterials, which would otherwise be degraded by plasma spray. In this work, two agglomerated hydroxyapatite powders, respectively with and without heat treatment after agglomeration, were cold sprayed for various spraying parameters. The cold spray process of pure HA coatings has been implemented through single track on two different biocompatible substrates: a metallic substrate (Ti-6Al-4V) and a polymeric substrate (poly (vinyl alcohol) (PVA)). The structure of the agglomerated HA powders and the corresponding features of the HA coatings were observed by SEM. For both types of substrates, it was shown that the agglomerated submicronic hydroxyapatite powders could lead to a homogenous layers of submicronic HA grains. In the case of particles without heat treatment, thick layers could be obtained due to the binding action of residual by-products of the chemical synthesis of HA particles. It was also shown that one HA layer remained adherent after immersion in water, thus enabling the fabrication of ceramic coated hydrogels.

1 Introduction

Hydroxyapatite (HA) ceramics are used to coat metallic dental and orthopaedic implants in order to achieve an osteo-active layer in direct contact with bony tissues [1-2]. The main conventional process is plasma spray of pure HA powder. However, the melting of HA during the plasma process drastically affects the phase composition and crystallinity of the HA coating. The spraying parameters have to be accurately controlled to maintain at least 50% of pure crystalline HA within the coating. Therefore, a solid state deposition process like cold spray of HA powder might have a great potential to achieve fully crystalline HA coatings. Moreover, other harmful thermal effects to the substrate from the plasma or from the hot particles could be avoided. Thus, HA by cold spray could also be envisaged favourably in case of thermosensitive polymeric biomaterials.

The literature about cold spray process applied to brittle and non-deformable materials like ceramics is not abundant. Ceramics like TiO_2, SiC WO_3 and HA were investigated with evidence of thick coating in case of TiO_2 [8-14]. However, some attempts to achieve HA coatings onto polymer substrates by cold spray have been reported [15-16]. In addition to the nature of the ceramic and its intrinsic mechanical properties, the role of powder morphology and grain size might play a key role to enable a solid state physical adhesion and consolidation to form a coating. In this context, ultrafine or nanostructured powders are of great interest. In this work, the cold spray process involving structured HA powders propelled at supersonic velocities was investigated in order to achieve an HA coating on both metallic and polymer materials of interest in biomedical industry.

Two agglomerated hydroxyapatite powders with submicronic primary grains, respectively with and without heat treatment after agglomeration were cold sprayed for various spraying parameters on metallic and polymeric substrates currently used in clinics. The main purpose was to investigate the role of the powder morphology and its degree of consolidation on the resulting impact behaviour and potential coating formation by the cold spray process.

The substrates studied here are made of metallic titanium alloy (Ti-6Al-4V) and thermoplastic polymer (poly(vinyl-alcohol) (PVA)), both of which are used as bulk materials for the reconstruction of hard and soft osteoarticular tissues. In the case of PVA, it is used in its hydrogel form composed of a cross-linked network of PVA macromolecules swollen with water. This kind of structure is very close to that of connective tissues. In particular, PVA hydrogels have been shown to form non-degradable hydrogels with a good history of biocompatibility [3]. Such PVA hydrogels are already used in clinic for cartilage replacement, and numerous researches are currently carried out to develop artificial meniscus, ligament, and intervertebral disc [4-7]. Coating with a bioactive ceramic coating is a promising way to strengthen the bone-implant interface of these PVA hydrogel implants. While the impacts and temperatures caused by cold-spray are certainly too severe for soft PVA hydrogels, they may be acceptable for dry PVA. Therefore, we propose to explore a two-step process to make PVA hydrogels coated by ceramics by firstly cold-spraying of HA on dry PVA and secondly swelling of the coated system in water.

2 Materials and methods

2.1 Powders and substrates

HA powders: Two types of hydroxyapatite powders were investigated. Commercial HA is synthetized with diamonium phosphate $(NH_4)_2HPO_4$ and calcium nitrate $Ca(NO_3)_2$ in distilled water with ammonium hydroxide NH_4OH to control the pH of the aqueous solution according to the following chemical reaction:

$$10\ Ca(NO_3)_2 + 6\ (NH_4)_2HPO_4 + 8\ NH_4OH \downarrow Ca_{10}(PO_4)_6(OH)_2 + 20\ NH_4NO_3 + 6\ H_2O$$

Then, filtration, atomization of the slurry and subsequent sieving led to a spherical agglomerated HA powder, namely the 'non-calcined HA' while further calcination and sintering at 1050 °C led to the corresponding 'calcined HA'. This latter HA powder is the commercial medical grade (25-60 µm) that could be used for plasma spray process but that was never used for cold spray. The purpose was to investigate the influence of the calcination/sintering consolidation of the starting HA powder on the resulting high velocity impact and potential HA coating formation. The particle size distribution (Malvern Mastersizer 3000) is summarized in **Table 1**. Both HA powders were with a similar range for the median size D_{50} with a narrow distribution range for the calcined HA while non-calcined HA was with a larger one.

Table 1: HA powders particles size (D in vol.%)

Particles	D_{10} (µm)	D_{50} (µm)	D_{90} (µm)
Calcined HA	27.6	41.8	61.4
Non-calcined HA	8.7	46.7	83.3

PVA substrates: Dry Poly (vinyl alcohol) (PVA) substrates were prepared by solvent-casting method. From PVA powder (Sigma-Aldrich), a 10wt% PVA aqueous solution was poured in Petri dishes and solvent was evaporated in vacuum-oven at 700 mbar and 80°C for 8h. Then it was cooled at room temperature for 12h. Translucid disks of dry PVA with thickness 540±170 µm were obtained. Dry PVA melting temperature is 225°C in air while PVA hydrogel after swelling completely dissolves in water after 1 hour upon heating above 85°C.

Ti-6Al-4V substrates: Ti-6Al-4V plates of $25\times25\times5mm^3$ were prepared with and without sand blasting preparation using 300µm white corundum. The average roughness was Ra=2.5 µm and 0.85 µm respectively.

2.2 Cold spray experiments

A high pressure cold spray apparatus (Kinetiks K3000,Oerlikon Metco, Switzerland) was used with nitrogen and MOC nozzle. The powder feedrate was 7±1 g/min. PVA disk specimen was solidly hold in order to expose a 40 mm diameter zone to the supersonic flow of gas and particles. Single track with one pass was achieved with nozzle speed at 10 mm/s. These experiments were achieved only varying the stagnation gas temperature (T) and pressure (P) with also the stand-off distance (SoD).

3 Results and Discussion

3.1 Characteristics of the HA powders

Both powders were observed by SEM (Nova NanoSEM 450, FEI). SEM images with various magnifications on free or mounted and cross-sectioned powder are given in **Fig. 1** pour non-calcined HA and **Fig. 2** for calcined powder respectively.

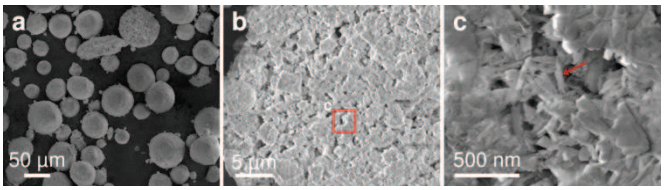

Fig. 1 SEM images non-calcined HA: a) free particles; b) details of crushed particle (SE Mode); c) zoom inside (b) with blocky and needle-like crystals.

Non-calcined HA (Fig. 1) exhibited a spherical shape with some porosity and inside grains with blocky or needle-like primary particles. Calcined HA (Fig. 2) is also spherical with submicronic grains fused and sintered together in a highly porous microstructure. A porosity level of 57% was estimated by quantitative image analysis (imageJ) on a polished cross-section.

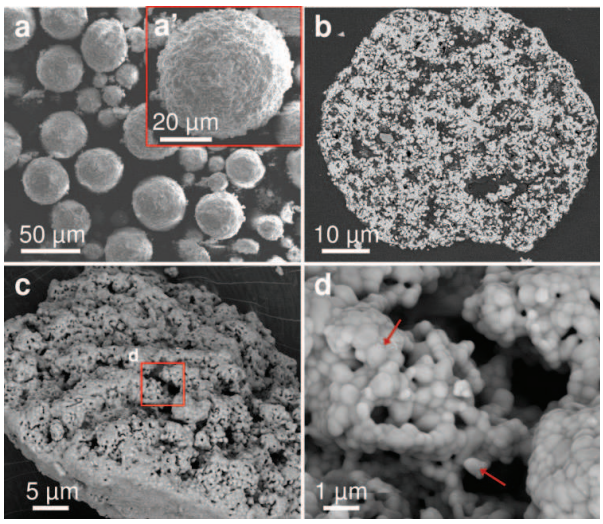

Fig. 2 SEM images of calcined HA: a-a') overview and details of free particles; b) Polished cross-section

(BSE mode); c) Crushed particle; d) Zoom inside (c) with submicronic fused/sintered particles.

The phase composition of both powders were analysed by X-ray diffraction (XRD) with CuKα radiation and Brucker D-500 diffractometer. Diffraction patterns ranging from 20 to 80° (step size 0.032°) are given in **Fig. 2**. Non-calcined HA was crystalline HA while calcined HA exhibited a few quantity of CaO.

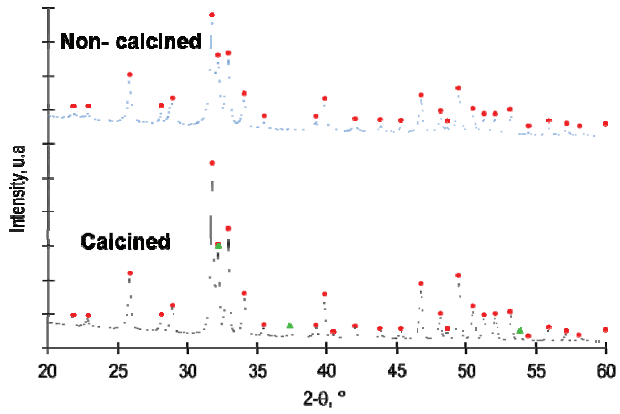

Fig. 3 XRD profiles of calcined and non-calcined HA powders, HA (#9-432) (●) and CaO (#37–1497) (▲).

FTIR analysis spectra (Bruker TENSOR 37 spectrometer) with 4 cm^{-1} resolution were carried out on HA pellets mixed with KBr. FTIR spectra of calcined and non-calcined HA particles are given in **Fig. 4**. Both powders exhibited typical 1100-900 cm^{-1} and 700-500 cm^{-1} bands for the phosphate groups v_3PO_4 and v_4PO_4 of apatite. In case of non calcined HA large absorption bands (3600 and 2800 cm^{-1}) are of absorbed water and bands centered at 1382 and 821 cm^{-1} correspond to NO^3 groups which are nitrate residues. Concerning the calcined powder, bands at 3647 and 3572 cm^{-1} correspond to the OH groups of calcium hydroxide ($Ca(OH)_2$). Another OH group is noticed at 630 cm^{-1}. Bands between 1550 and 1420 cm^{-1} and between 900 and 850 cm^{-1} are v_3CO_3 and v_2CO_3 groups of apatite carbonates.

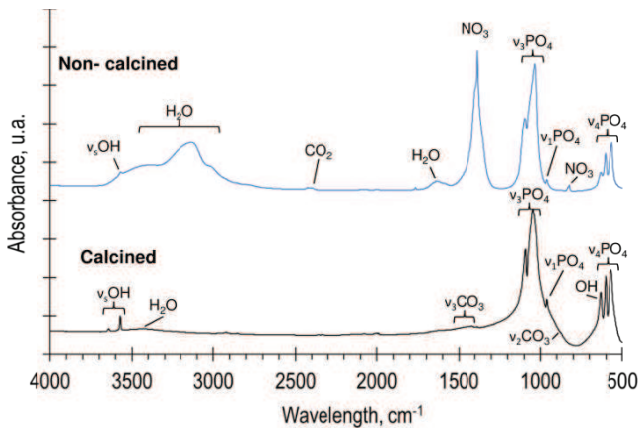

Fig. 4 FTIR spectra of calcined and non-calcined HA

3.1 Cold spray of calcined HA

Ti-6Al-4V substrates: In Fig.5 , Non Blasted (NB) and Sand Blasted (SB) Ti-6Al-4V substrates were investigated using both T=230 °C, P=1.0 MPa (A and C in Fig. 5), or T=200 °C , P=3.0 MPa (B and D in Fig. 5) with similar SoD=30 mm. From these observations, it evidenced the beneficial influence of roughness to achieve thin layer (~ 2-3 µm) of HA without spalled areas.

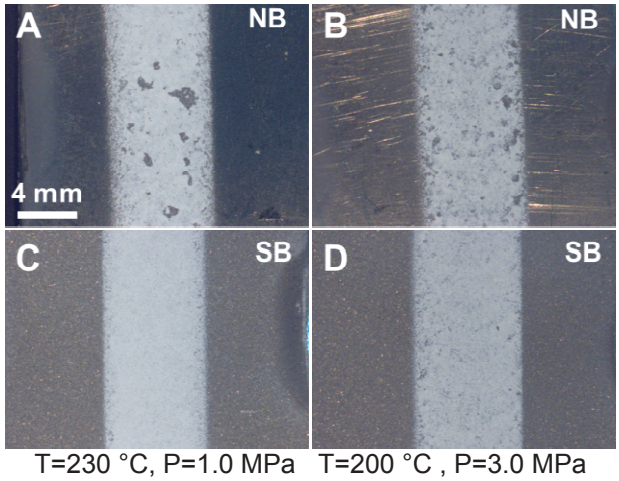

Fig. 5 Top surface macroscopic views of calcined HA coatings on Non Blasted or Sand Blasted Ti-6Al-4V

Low temperature and pressure are enough to create an adhesive layer that consisted in a distribution of submicronic particles that were present in the starting porous and agglomerated powder (see Fig. 6.). The calcination/sintering process did not consolidate too much the primary HA particles together. Therefore they were easily separated and released during impact. This type of powder morphology might be used to taylor specific powder that can initiate original fragmentation and consolidation mechanisms that could be suitable for pure ceramics. Further consolidation between particles would be needed to get thicker coating. Such consolidation process are drastically influenced by the particle size which are submicronic and not nanometric in our case.

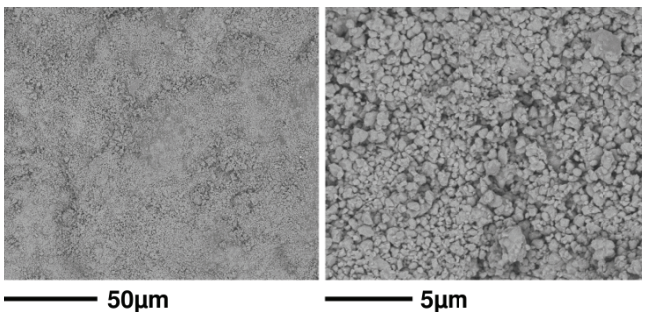

Fig. 6 Top surface SEM-BSE views of calcined HA coatings on SB Ti-6Al-4V (T=230 °C, P=1.0 MPa)

Dry PVA and PVA hydrogels substrates: Typical overviews after cold spray of calcined HA (T=200 °C,

P=1.0 MPa, SoD=30 mm) are given in Figures 7a and 7b in case of PVA hydrogel and dry PVA substrates respectively. It was obvious that swollen PVA substrate was fully damaged and completely flowed away by the gas stream and sprayed powder. Conversely, the dry PVA substrate resisted and a layer of HA was obtained without any macroscopic evidence of degradation. The white HA coating seemed homogeneous and adherent to the substrate.

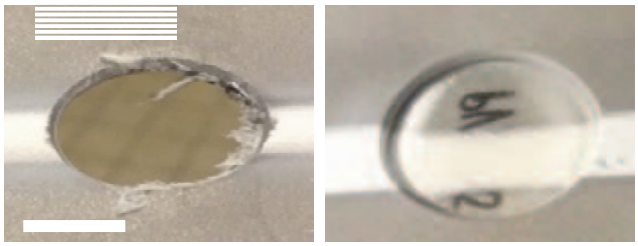

Fig. 7 Top surface macroscopic views of calcined HA deposited on a) hydrogel PVA; b) dry PVA

Other spraying parameters were further investigated only in case of dry PVA. These experiments are summarized in Fig. 8. The main limitation to achieve one HA layer is thermal degradation of the dry PVA substrate that turned brown. For the shorter stand-off distance, the temperature of the stagnation gas can be varied between 200 and 250°C for a pressure of 1 MPa without macroscopic evidence of substrate degradation. When the pressure is increased to the maximum of K3000, one HA coating can be still obtained for the lowest temperature of 200°C. Even if temperature higher than 250°C could be applied with longer stand-off distance, it did not drastically modify the damaging response of the PVA to the thermal flux except for SoD = 150 mm. For this latter, damaging effects were avoided and high energy parameters (T=300°C and P=2.0 MPa) could be applied. In the following, the PVA/HA interface and other HA coating's features for the lowest temperature (T=200°C) and pressure (P=1.0 MPa) at short spraying distance (SoD=30mm) were characterized and discussed.

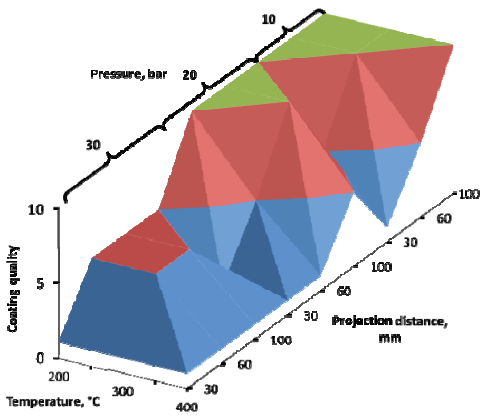

Fig. 8 Influence of main CS parameters on HA deposition and thermal degradation of dry PVA

From fractographic and top surface observations by SEM (Fig. 9) , it could be seen that an homogeneous HA layer could be obtained in the middle of the track. At the boundary, where fewer impacts occurred, single craters were obvious and evidenced the large deformation of the dry PVA substrate upon impacts. In case of biomedical applications, this roughening effect might be beneficial. Moreover, it can be observed that small HA particles were still attached in the centre of craters while PVA was ejected at the rim of the craters.

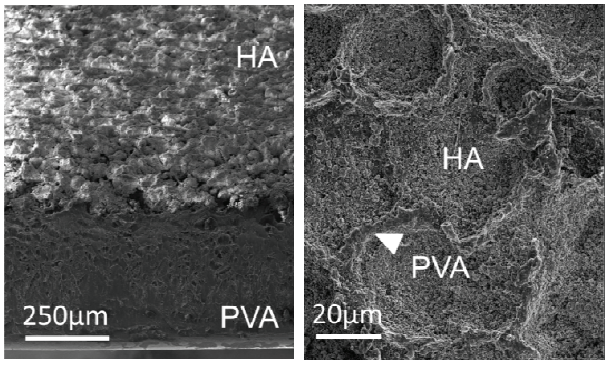

Fig. 9 SEM fractographic and top surface views in the centre (left) and at the boundary (right) of the HA track

The HA/PVA interface was observed by SEM at higher magnification (Fig. 10). The presence of submicronic primary HA particles that were released upon impact when calcined HA porous and agglomerated particles were broken. PVA was probably affected by heat during cold spray. Therefore HA submicronic particles seemed to be physically and strongly bonded to PVA.

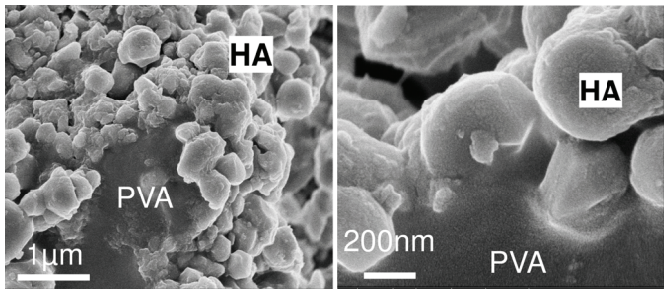

Fig. 10 SEM views of HA/PVA interface within a crater

The excellent adhesion of HA onto dry PVA was confirmed after swelling of the HA/PVA coating. The HA coating on dry PVA substrate was immersed in ultra-pure water for a week at 37 °C under magnetic stirring to reach a 50% equilibrium content of water in PVA. After this immersion period, it was observed that the PVA hydrogel obtained after swelling remained fully covered by the HA coating. This macroscopic observation was confirmed by SEM observations using BSE detector and low vacuum mode, which allow observations of hydrated PVA samples without sample preparation (Fig. 11). HA/PVA hydrogel was obtained and could be envisaged for biomedical application.

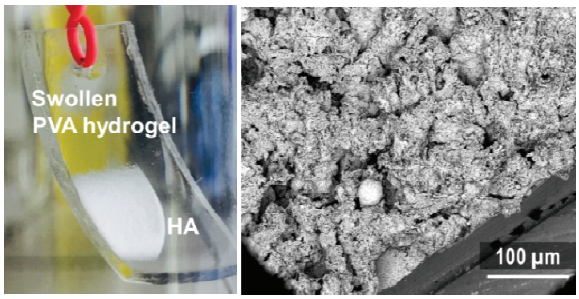

Fig. 11 HA/PVA hydrogel after 1 week immersion

3.2 Cold spray of non-calcined HA

Non-calcined HA powder was cold sprayed using similar parameters than for calcined HA powder (T=200°C, P=1.0 MPa, SoD =30 mm) and also by implementing a single track with one pass. A macroscopic view of the top and the side of a HA/Ti-6Al-4V specimen is given in Fig. 12. A very thick (~500µm) and homogenous HA coating was obtained on Ti-6Al-4V. Similar results were obtained on Dry PVA. The coating was very dense but with rather poor cohesion. From the macroscopic top surface view, it can be seen that two phases are coexisting within the HA layer.

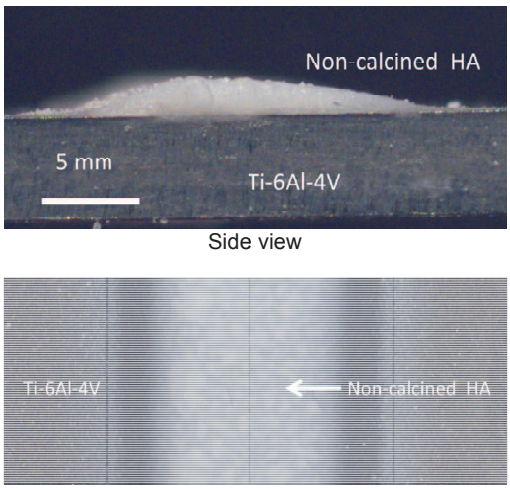

Fig. 12 Macroscopic views of non-calcined HA/Ti-6Al-4V specimen

It was confirmed by SEM observation (Fig. 13) where HA particles are present and surrounded by a glassy compound. This compound is probably made of hydrated nitrates species as by-products of the HA synthesis that were detected by FTIR in the starting non-calcined powder. Differential scanning calorimetry and thermogravimetric analyses confirmed the presence of a large amount (30% of mass loss) of a compound that degraded below 400°C. Such nitrates compounds are not degraded during cold spray and act as a binder within the coating and probably with the surface.

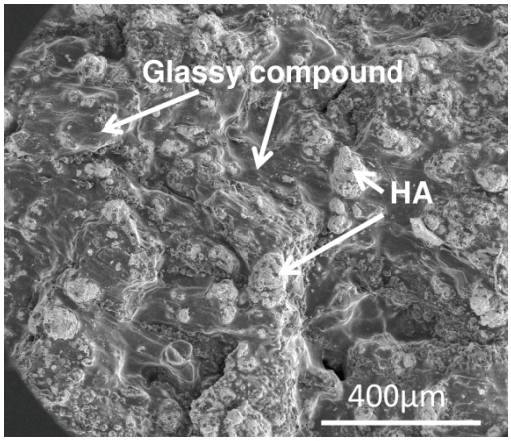

Fig. 13 SEM surface view non-calcined HA coating

4 Conclusion

In this work, the cold spray process was investigated in order to achieve an HA coating from two agglomerated and porous hydroxyapatite powders both with submicronic primary particles, respectively calcined and non-calcined. Two different types of substrates, metallic (Ti-6Al-4V) and polymeric (PVA) materials were also investigated because of their interests in implantology. It was found that both substrate materials exhibited a similar behaviour for both powders upon impact using low temperature and pressure.

The calcined HA powder broke during impact and released the submicronic primary particles that were previously agglomerated and probably poorly sintered in this case. The resulting film was made by a dense distribution of the submicronic particles. The roughness of the metallic substrate is beneficial to the adhesion. In case of PVA, deep craters that were formed by the HA particles increased the roughness during cold spray but no thermal degradation occurred macroscopically. In this case, a strong HA/PVA interface was obtained for each submicronic HA particle because of local heating of the PVA from the gas stream during impact. Thus, HA coated dry PVA could be swollen to form an original HA/PVA hydrogel coating without loss of HA when immersed for one week in water.

The non-calcined HA powder led to very thick (~500µm) that was very dense but with rather poor cohesion and adhesion. The HA deposit exhibited HA particles surrounded by a glassy compound which was probably the hydrated nitrates by-products remaining in a large amount in the non-calcined starting powder Such hydrated nitrates compounds are not degraded during cold spray and act as a binder within the coating and probably with the surface. Such experimental results could be used to discuss the design of powder involving rather low temperature binder that could be included in the starting powder to help the ceramic coating formation.

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