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Comparison between Suspension Plasma Sprayed and High Velocity Suspension Flame Sprayed bioactive coatings

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ABSTRACT

This paper assesses the diverse potentialities of two different suspension spraying processes, namely High Velocity Suspension Flame Spraying (HVSFS) and Suspension Plasma Spraying (SPS), for the deposition of bioactive coatings based on hydroxyapatite and on a new, custom-made K_2O–Na_2O–CaO–P_2O_5–SiO_2 bioactive glass. With both feedstock types, the HVSFS process imparts high in-flight velocities to the particles and aggregates released after solvent vaporisation, resulting in well flattened, tightly bound lamellae. The coatings, <50 μm thick and very dense, have hardness and elastic modulus values close to those of the corresponding bulk materials. They can be employed as high-quality bioactive layers on metallic implantable devices. Few days of soaking in simulated body fluid (SBF) results in the re-precipitation of a surface hydroxyapatite layer, albeit through different mechanisms. In HVSFS bioactive glass coatings, ion leaching turns the surface into a silica gel, onto which hydroxyapatite subsequently deposits. In HVSFS hydroxyapatite, the amorphous fraction is progressively dissolved and microcrystalline hydroxyapatite precipitates onto the remaining coating layer.
The SPS technique, due to the lower in-flight velocity of particles and agglomerates, always produces more porous, rougher layers with columnar-like growth. They are not mechanically strong, but their peculiar structure can be useful for specific, functional applications. The high surface area of porous SPS bioactive glass coatings favours ion leaching and fast dissolution in simulated body fluid (SBF); hence, it is suggested that SPS bioglass could be useful as a rapidly resorbable layer. SPS hydroxyapatite, by contrast, is more stable than the corresponding HVSFS layer, despite its porosity, because of the higher crystallinity. After the amorphous fraction is dissolved in SBF, newly formed hydroxyapatite does not constitute a surface layer but precipitates inside the pores, suggesting that a sealing pre-treatment in SBF could be a means to tune porosity and phase composition.

1. Introduction

Titanium and its alloys are extensively used as biomaterials for orthopaedic and dental applications (i.e. joint and hip replacements, pins, screws for fracture fixation, bone plates, etc.) due their biocompatibility, excellent corrosion resistance, lower density than other metallic biomaterials and suitable mechanical properties [1–4]. However, these materials do not form a chemical bond with bone after implantation, and the human body encapsulates them in a fibrous capsule to isolate them from the surrounding tissue. In order to promote osseointegration, the surface of titanium and its alloys is often coated with hydroxyapatite (HA), a calcium phosphate ceramic that is similar to the mineral phase of bone [5–8]. Although several methods are currently available to produce HA coatings, such as sputtering, electrophoretic deposition, sol–gel processing, pulsed laser deposition, etc. [9–15], the only commercially accepted technique is the conventional atmospheric plasma spray process. It consists of injecting a dry powder feedstock into a thermal plasma jet, which heats the particles and accelerates them towards the substrate, where they impact, flatten and get deposited in the form of lamellae (also called "splats") [8,9,16,17]. In spite of its high productivity, relatively low cost and moderate heat input conveyed to the substrate, this process has a series of drawbacks, including possible chemical and structural alterations of crystalline bioactive ceramics (such as HA) and the inability to deposit thin (<50 μm thick) coatings [18]. In particular, as the processing temperature increases, HA can be decomposed to tricalcium-phosphate and to tetracalcium-phosphate; the formation of CaO can also be observed as a result of thermal degradation [18–21]. On the other hand, the need for thin coatings is emerging in the field of bioactive ceramics as a large thickness is not only superfluous in order to impart osseoconductive or even osseoinductive properties to the coated surfaces, but it is also detrimental to adhesion and long-term mechanical stability [22]. A high thickness is indeed likely to induce relevant deposition stresses, which

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undermine the adhesion and may cause long-term de-bonding between the coating and the substrate, resulting in the implant failure and/or in the release of undesirable debris in the surrounding tissues [18,23].

The innovative suspension thermal spray techniques [24–26] are ideally suited to deposit thin layers and, on the other hand, they share the common fundamental advantages of all thermal spray processes. Namely, in comparison to alternative deposition techniques, they feature high productivity and relatively low processing cost, including the fact that the coatings do not need any post-deposition heat treatment for consolidation, as it occurs e.g. in the case of electrophoretic coatings of pure HA [27–29]. Since in the suspension thermal spray process the feedstock is dispersed in a liquid medium, which ensures good flowability, the particle size distribution of the powder can be much finer than in conventional atmospheric plasma spraying, resulting in thinner lamellae. Both in conventional thermal spraying and in suspension thermal spraying, the coating consists of the superposition of a certain number of lamellae, but in the latter case, since the splat thickness is much lower, the minimum thickness limit for the coating is reduced; hence, deposits of less than 50 μm can be obtained.

More specifically, two of the available suspension thermal spray processes, High-Velocity Suspension Flame Spraying (HVSFS) and Suspension Plasma Spraying (SPS), have already shown their potential for the manufacturing of bioactive coatings.

The High-Velocity Suspension Flame Spraying (HVSFS) [30–32] technique employs a modified gas-fuelled high velocity oxygen-fuel (HVOF) torch in order to process the liquid suspension. As the latter is axially injected inside the combustion chamber of the torch, complete mixing of the suspension drops with the gas is favoured. The solid particles (released after solvent vaporisation) are heated by the gas in the combustion chamber and in the expansion nozzle and, as the gas stream attains supersonic velocity upon expansion to ambient pressure outside the torch, they are also dragged to extremely high velocities (up to 900 m/s according to some recent estimates [33,34]). Extensive flattening onto the substrate is achieved, resulting in very dense layers with high cohesive/adhesive strength, which has already been experimentally verified both for calcium-phosphate coatings (tricalcium phosphate [34] and hydroxyapatite [31]) and for bioactive glass coatings [35]. The latter, even though somewhat prone to crystallise at high temperature, offer several advantages with respect to HA [13,36–38], since they do not decompose during thermal spraying and they possess a higher bioactivity index than HA. Among bioactive glasses, 45S5 Bioglass®, first proposed by Prof. Hench at the end of the 1960s [6], is the most bioactive one and it is able to bond both to bone and to soft tissues. Recently the ability of 45S5 Bioglass® to induce neovascularisation and to promote stem cell differentiation into osteoblasts has also been stated [39,40].

The Suspension Plasma Spraying (SPS) process injects the liquid suspension into a thermal plasma jet, issuing out of a standard atmospheric plasma spraying torch [24,25,41]. Due to the radial injection scheme, and to the periodic fluctuations in plasma energy, liquid drops follow very different trajectories in the gas stream [41–43]. The particles therefore reach the substrate with a wide range of temperatures and velocities. In an attempt to overcome this issue, recent research has investigated the design of "resonant-mode" torches where a "drop-on-demand" injector is synchronised with a plasma operating with regular, periodic pulsations [44,45]. However, such devices are not yet available on the market; hence, most research is still carried out using "standard" atmospheric plasma torches.

Moreover, under typical thermal plasma conditions, the gas mean free path of ~0.4 μm (according to [46]) is comparable to the size of micrometric or sub-micrometric particles. This gives rise to non-continuum effects, also known as Knudsen effect, which drastically decrease the heat and momentum transfer from the gas to the particles [46–48]. This issue does not affect the HVSFS process, because the high-pressure and low-temperature gas (compared to a thermal plasma) possesses lower mean free path [46]. Considering that the plasma is also strongly cooled by the suspension solvent evaporation, the result is that particles are poorly heated and are accelerated to much lower velocities than with the HVSFS process. SPS coatings are therefore typically more porous and rougher than HVSFS ones. Their microstructure is further modified by the extremely large heat flux which a thermal plasma jet delivers at the short stand-off distances (often comprised in the 30–60 mm range) used in the SPS process. Quantitative calorimetric measurements have indeed returned values from 2–8 MW/m^2 [49] up to maxima of 20 MW/m^2 [46,50,51], 25 MW/m^2 [52] or even 37 MW/m^2 [53], compared to values of <1 MW/m^2 for conventional atmospheric plasma spraying at stand-off distances of ≈100 mm [49,52]. Such heat fluxes are likely to induce sintering of the deposited material, which was shown in [51,54] and numerically demonstrated in [55], based on the solid-state diffusion theory.

The microstructures of SPS ceramics therefore frequently exhibit peculiar features, such as the co-existence of flattened lamellae together with regions made up of sintered, unmelted particles [54,56,57]. The porosity of these coatings also differs considerably from that of conventional atmospheric plasma sprayed ones. Whilst the latter contains larger, micrometric pores and elongated inter- and intra-lamellar microcracks, SPS coatings typically contain numerous, rounded, sub-micrometric pores [58]. The distribution of all microstructural features in SPS coatings is further sensitive to the properties of the suspension (average particle size, dispersion, etc.) [56,57].

On the other hand, the SPS technique is highly versatile and flexible and, differently from the HVSFS process, there is no risk to build up crusts of material on the inside of the torch, which is a known source of defects in the coating due to the periodic ejection of fragments of the crust [59]. Due to such flexibility, the SPS technique has already been proposed for a large variety of functional applications, including the manufacturing of gas-sensing layers [60], of solid oxide fuel cells [61], and of thermal barrier coatings [62]. The latter example also shows an instance where porous SPS coatings prove to be advantageous over denser HVSFS ones, because of better compliance (resulting in enhanced thermal shock resistance) and lower thermal conductivity. Several authors have also considered the use of SPS for the deposition of bioactive glass coatings of various compositions, with promising

Table 1
SPS process parameters for the deposition of the BG-Ca/Mix and HA suspensions.

Material	BG-Ca-Mix				Hydroxyapatite			
Parameter set	#1	#2	#3	#4	#1	#2	#3	#4
Ar flow rate (SL/min)	40	40	50	50	40	40	50	50
H_2 flow rate (SL/min)	10	10	10	10	10	10	10	10
Arc current (A)	600	600	600	600	600	600	600	600
Suspension feed rate (g/min)	42	42	42	42	47	47	47	47
Stand-off distance (mm)	60	60	60	80	60	60	60	80
Traverse speed (mm/s)	500	500	500	500	500	500	500	500
Pass spacing (mm)	3	3	3	3	3	3	3	3
Number of torch cycles	8	2	2	2	2	4	4	4
Max. deposition T (°C)	732	538	485	477	405	500	616	357

Table 2
HVSFS process parameters for the deposition of the BG-Ca/Mix and HA suspensions.

Material	BG-Ca-Mix					Hydroxyapatite
Parameter set	#1	#2	#3	#4	#5	#1
Propane flow rate (SL/min)	55	45	45	55	50	55
Oxygen flow rate (SL/min)	350	300	350	300	325	300
Suspension feed rate (g/min)	77	77	77	77	77	105
Stand-off distance (mm)	120	120	100	100	110	100
Traverse speed (mm/s)	600	600	600	600	600	600
Pass spacing (mm)	2	2	2	2	2	2
Number of pre-heating cycles	4	4	4	4	4	4
Number of deposition cycles	1	1	1	1	1	1
Max. deposition T (°C)	266	239	237	345	227	≈300