

# Some Problems Associated with Thermal Sprayed Ha Coatings: A Review

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**Abstract**—New promising techniques for depositing hydroxyapatite (HA) coatings on bio-implants are continuously being investigated. This review will focus on the inadequacies of various thermal spray techniques used for the deposition of HA coatings on bio-implants. From the studies observed in the literature, some problems are associated with HVOF, plasma spray and flame spray techniques. However, problems cited with the thermal spray techniques include variation in bond strength between the coatings and the metallic substrate, porosity and amount of crystallization of coating powder after deposition. Biological responses of these coating techniques are also critically reviewed.

**Keywords:** Hydroxyapatite, Plasma spray, Biological response

## INTRODUCTION

Hydroxyapatite (HA) coating has received wide attention of researchers in orthopaedics in recent years due to its excellent biocompatibility and osseointegration ability in body environment. Hydroxyapatite coatings have good potential as they can exploit the mechanical properties of substrate such as stainless steel (SS-304 L and 316 L) and titanium alloys (pure Ti and Ti-6Al-4V), while utilising the biocompatibility and bone bonding properties of the ceramic. Various deposition techniques, such as sol-gel [1,2], sputtering [3,4], pulsed laser deposition [5], and thermal spraying [6–8], are available for the deposition of HA coatings. Of the various techniques used, only thermal spraying, in particular, plasma spraying is the only commercially accepted method by Food and Drug Administration (FDA), USA for producing hydroxyapatite coatings.

From the last several years, continuous research on HA coatings have not only focused on tissue-coating interface, but also on the problems associated with the coating process and optimization of coating properties for maximum tissue response [9]. The current method used by many vendors for depositing HA coatings on metallic implant substrates are the plasma spraying or arc plasma-spraying process [10,11]. Food and Drug Administration guidelines have been described minimal requirements for HA coats [9,12,13] see Table 1.

Advantages of thermal spraying include a rapid deposition rate and a sufficiently low cost [10,11]. However, problems cited with the thermal sprayed coatings include deviation in bond strength between the coatings and the metallic substrates [14], variations in HA structure due to the coating process [15,16] and poor adhesion between the coatings and metallic substrates [14]. As in the case of the adhesion between the thermal

sprayed coatings and the metallic substrates, the nature of the substrate plays an important role. The bonding of the thermal sprayed HA coatings appear to be entirely mechanical in nature. As verified in several studies, a highly roughened substrate surface exhibited higher bond strength as compared to a smooth substrate surface [17]. Knowing the problems observed with HA coatings obtained using the various thermal spraying process, numerous experimental deposition process have been investigated, including plasma spraying, HVOF and flame spray technique [18, 19]. However, given the vast number of experimental deposition process, this review will focus only on HA coatings produced using the different thermal spray processes.

Table 1: HA Coating Requirements [Ref. 16,17]

Property	Specification
Thickness	Not Specific
Crystallinity	62% Minimum
Phase purity	95% Minimum
Ca/P ratio	1.67-1.76
Density	2.98 g/cm <sup>3</sup>
Heavy metals	<50 ppm
Tensile Strength	>50.8 MPa
Shear Strength	>22 MPa
Abrasion	Not Specific

## THERMAL SPRAY TECHNIQUES USED TO PREPARE HA COATINGS

### HVOF Spray Process

In HVOF spraying, heat is produced by burning mixture of oxygen and fuel such as hydrogen, kerosene, propane, propylene, natural gas, ethylene, or acetylene. Due to the special nozzle design, a jet with supersonic speed is produced. The ability to produce dense coatings with low amount of degradation, oxidation of metallic materials, and phase transformations is the main feature of the

HVOF process. This is due to the short dwell time of the particles in a relatively cold flame. It is widely used to produce cermet and metal coatings, but the HVOF process has also been demonstrated to be able to deposit dense ceramic coatings.

In the HVOF process, fuel and oxygen are introduced to the combustion chamber together with the spray powder. The combustion of the gases produces a high temperature and high pressure in the chamber, which causes the supersonic flow of the gases through the nozzle. The powder particles melt or partially melt in the combustion chamber and during the flight through the nozzle. The flame temperature varies in the range of 2500 °C–3200 °C, depending on the fuel, the fuel gas/oxygen ratio and the gas pressure. In the HVOF process the particles melt completely or only partially, depending on the flame temperature, particle dwell time, material melting point and thermal conductivity. A schematic diagram of the HVOF process is presented in Fig. 1.

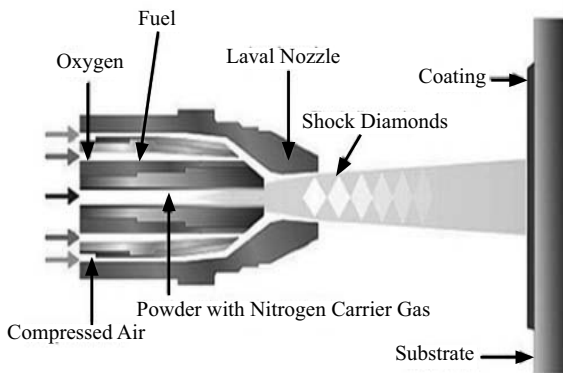


Fig. 1: HVOF Process

However the drawback of this technique is that coating is not 100% crystalline [20]. Parameters for HVOF Spray are given in the Table 2.

### Plasma Spray Process

The plasma spray process uses a DC electric arc to generate a stream of high temperature ionised plasma gas, which acts as the spraying heat source. A schematic diagram of plasma spray is shown in Fig. 2.

The cooling material, in powder form, is carried in an inert gas stream into the plasma jet where it is heated and propelled towards the substrate. Because of the high temperature (15000°C) and high thermal energy of the plasma jet, materials with high melting points can be sprayed.

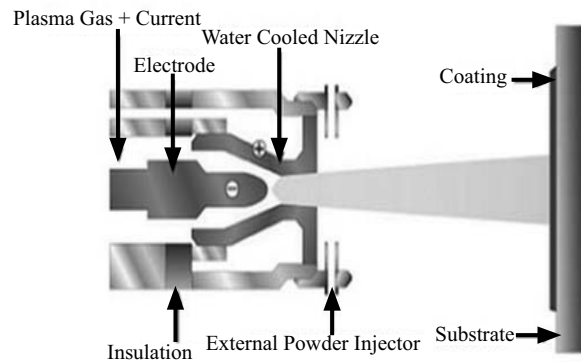


Fig. 2: Plasma Spray Process

The plasma gun comprises a copper anode and tungsten cathode, both of which are water cooled. Plasma gas (argon, nitrogen, helium) flows around the cathode and through the anode which is shaped as a constricting nozzle. Plasma spraying has the advantage that it can spray very high melting point materials such as refractory metals. But main weakness of this technique is the generation of amorphous calcium phosphate and bioactive calcium phosphate phase such as tetra calcium phosphate (TTCP), tri-calcium phosphate (TCP) and meta-stable crystalline products such as oxy-hydroxyapatite which may cause mechanical and adhesive instabilities of the coating [20]. Optimized parameters for plasma spray are given in the Table 2.

Table 2: Spray Parameters of HVOF and Plasma Spray [Ref. 21]

HVOF	Plasma Spray
Flow of H <sub>2</sub> : 566 l/min	Net energy: 2 kW
Flow of O <sub>2</sub> : 283 l/min	Flow of Ar: 28.30 l/min
Spray distance: 250mm	Flow of He: 18.87 l/min
Flow of Ar (powder carrier gas): 19 l/min	Flow of Ar (powder carrier gas): 9.43 l/min
Powder feeding rate: 8 g/min	Powder feeding rate: 8 g/min

Plasma spraying is becoming the main process of the thermal spray methods and is commonly used to apply hydroxyapatite to dental implants and orthopaedic prostheses. Powder is injected into the plasma flame and accelerated to about 200 m/s before impacting the substrate [27, 28]. These high impact velocities supply kinetic energy which is expended in spreading the molten droplet and creating lamellae with a large surface area. The large contact area with the substrate associated with the lamellae facilitates rapid heat transfer which may be sufficient to form the amorphous phase. The rapid solidification arising from the high cooling rates in plasma spraying has produced amorphous phases from pure ceramics such as alumina, eutectic compositions of ceramic components such as alumina-zirconia and iron based alloys [29] or cobalt-tungsten-carbon [30].

## Flame Spray Process

Among the thermal spray methods, the simplest and the cheapest way to deposit coatings in flame spraying. A schematic diagram of flame spray is shown in Fig. 3.

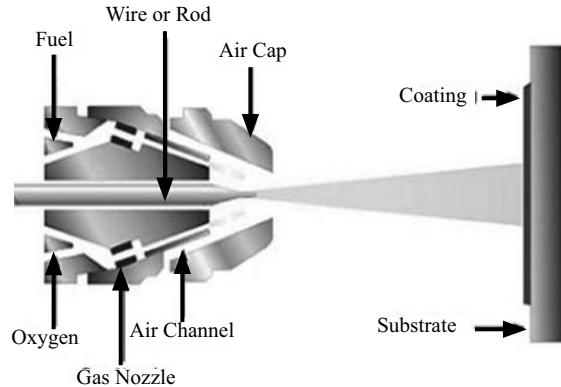


Fig. 3: Flame Spray Process

Both wire and powder can be used as a coating material. The process relies on the chemical reaction between oxygen and a fuel of combustion (acetylene, hydrogen) to produce a heat source. This heat source creates a gas stream. The feed stock material to be sprayed is fed into the flame in the form of a wire and compressed air is then used to atomize the molten metal and accelerate particles onto the substrate.

The flame spray process is limited by materials with higher melting temperatures than the flame can provide or if the material decomposes on heating. Because of the low flame temperature and particle velocity, coatings are usually porous and bond strength of deposits is low as well as adhesive & shears strength between coating & substrate [31].

## MAIN CHARACTERISTICS OF THERMAL SPRAY TECHNIQUES

### Crystallization

The crystallinity of the coatings is evaluated using the following equation:

$$\text{Crystallinity (\%)} = A_{\text{HA}}/A_{\text{C}} \times 100\% \quad (1)$$

where  $A_{\text{HA}}$  is the area under the HA peaks, and  $A_{\text{C}}$  is the area under all peaks [32]. The problem associated with thermal spraying methods is the decomposition of HA coatings during spraying to form secondary phases such as oxy-hydroxyapatite (OHA), tetracalcium phosphate (TTCP),  $\alpha$ - and/or  $\beta$ -tricalcium phosphate ( $\alpha$ -TCP,  $\beta$ -TCP), amorphous phase and calcium oxide (CaO). The decomposition is related to the high temperature of thermal spraying flame. For that, a careful control of thermal spraying parameters is required to prevent the decomposition and get high crystalline HA coatings [32].

The biocompatibility and the mechanical properties will depend on the coating microstructure, crystallinity and phase composition. It has been generally accepted that high dissolution rates are unwanted because the dissolution of the secondary phases in the body fluids weakens the coating structure. In order to achieve fixation with surrounding bone and a long life, the HA coating must have limited dissolution after implantation. Therefore the crystallinity of the coating is a very important parameter [23]. Post-heat treatment for sprayed HA coatings is a good method to minimize these phases and increase the crystallinity, as well as reduce the residual stress of HA-based coatings with the aim to promote the resorption resistance [33].

### Adhesive Strength and Porosity

The adhesive strength between the HA coatings and the metallic implant should be maximized to avoid cracking, spalling, and chipping of the HA coating during emplacement of the implant. Improving the adhesion properties is related to increasing the bonding strength of HA particles, as well as the adhesive strength at the interface between the HA coat and the metallic implant [25]. The bond strength of the HVOF-sprayed HA coating is higher than bond strengths of HA coatings deposited via air plasma spray, which generally exhibited bond strengths values below 20 MPa. The bond strength of the HVOF-sprayed HA coating is also higher than the bond strengths of vacuum plasma sprayed HA coatings, which exhibited bond strengths from 4 to 14MPa. According to the standard ISO 13779-2 'the bond strength of an HA coating shall have a value not less than 15MPa [23].

Plasma spray is one of the most used techniques due to numerous advantages such as simplicity, high deposition rates, low substrate temperature, variable coating porosity, phases, and structure. The main problem in plasma-sprayed HA coatings is the generation of amorphous calcium phosphate (ACP) and bioactive calcium phosphate phase such as tetra calcium phosphate (TTCP), tri-calcium phosphate (TCP), metastable crystalline products such as oxy-hydroxyapatite or oxy-apatite and the formation of CaO. The presence of large amounts of ACP is undesirable since its strong in vivo resorption may cause mechanical and adhesive instabilities of the coating [34, 35]. Although the plasma-sprayed HA coatings on titanium alloy implants show strong bonding between the HA coating and the bone structure, it has been recognized that the mechanical stability of the interface between the HA coating and titanium alloy substrate could be a problem either during surgical operation or after implantation. It cannot be used at highly loaded places such as femoral and tibial cortical

bones due to the brittleness of HA. One way to circumvent this inherent deficiency is to form HA-based composites by reinforcing with a mechanically superior secondary phase [26]. Typical values of the adhesive bond strength and porosity are given in Table 3, which are obtained after depositing by various thermal spray techniques.

**Table 3: Adhesion Strength and Porosity of HA Coatings Deposited by Different Thermal Spray Techniques**

Technique	Composition	Adhesive Strength (MPa)	Porosity	Ref.
HVOF	HA	37.5 ± 4.8	13 ± 2%	[22]
	HA (Nano-structured)	24 ± 8	1.4 ± 0.1%	[23]
	HA + TiO <sub>2</sub>	27 ± 1.51	----	[24]
Plasma Spray	HA + SiO <sub>2</sub> + Ti	7.5	----	[25]
	HA + Ti-6Al-4V	27.38	15.82 %	[26]
	HA	18.46	18.94 %	[26]

## BIOLOGICAL PERFORMANCE

The application of hydroxyapatite as coating on titanium alloy substrates has been widely used for clinical applications due to its excellent osteo-integration properties. The distinctive biocompatibility of HA and superior mechanical properties of the titanium alloy makes it an ideal choice for most biomedical applications. Under simulated physiological conditions, the in vitro characteristic of the plasma sprayed HA coatings are investigated by many researchers.

Kweh *et al.* has been observed that as-sprayed plasma sprayed HA coatings exhibited enhanced biological response as compared to heat-treated coatings. In vitro chemical and morphological changes on the as-sprayed and heat-treated coatings are found to occur. Complete dissolution of secondary phases such as CaO, TCP and TTCP are found to occur after 2 weeks of immersion due to their high ionic solubility product. Mechanical properties of the incubated coatings in SBF are found to deteriorate with immersion period. However, the heat-treated coatings exhibited superior mechanical stability than the as-sprayed coatings, indicating that structural integrity of the former coating are not as severely affected as the latter in physiological environment [36].

R.S. Lima *et al.* reported that a uniform layer of apatite (~35 µm) was formed on the HA coating after 7 days of incubation in SBF. Comparing to air plasma sprayed conventional HA coating, under the same SBF testing conditions, exhibited an apatite layer of ~20 µm. This characteristic apparently indicates a higher bioactivity and an accelerated nucleation of the apatite on the HVOF sprayed nanostructured HA coatings [23].

## CONCLUSION

The main problem associated with thermal spray techniques used for depositing HA coatings is the formation of secondary phases such as oxy-hydroxyapatite (OHA), tetracalcium phosphate (TTCP),  $\alpha$ -and/or  $\beta$ -tricalcium phosphate ( $\alpha$ -TCP,  $\beta$ -TCP), amorphous phase and calcium oxide (CaO). The HVOF is a higher temperature, higher velocity technique which is thought to impose a higher degree of melting on the bio-ceramic powders. It is concluded that the higher crystallinity and lower residual stress found in plasma spray coatings will result in a slow rate of dissolution in vitro relative to HVOF coatings.

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