Preliminary Study of Plasma Sprayed Hydroxyapatite Coating of Injection Moulded Cobalt based Femoral Hip Stem

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Abstract – Coating of the implant has specific functions ranging from improving fixation by establishing strong interfacial bonds, shelding the metallic implant from environmental attack or leaching effects and promoting fast tissue growth. Some important coating characteristics that are generally expected of biomedical coatings are good biocompatibility of the desire phase and crystallinity, good coating integrity and adequate porosity. In this paper, hydroxyapatite coating of newly developed injection moulded hip stem prototype has been evaluated and discussed. The effect of current during plasma spray process has been investigated.

Index Terms – Metal Injection Moulding, hip stem, hydroxyapatite, coating, plasma spray.

1. INTRODUCTION

Coating of the implant has specific functions ranging from improving fixation by establishing strong interfacial bonds, shelding the metallic implant from environmental attack or leaching effects and promoting fast tissue growth. Some important coating characteristics that are generally expected of biomedical coatings are good biocompatibility of the desire phase and crystallinity, good coating integrity and adequate porosity [1,2].

A bioceramic commonly used as coating material for metallic implants is hydroxyapatite (HA). HA has a similar chemical and phase composition to a living bone . It has been known to form a strong biological bond with bony tissue without the presence of soft fibrous tissues. The popular technique of the HA coating deposition that is used in the industrial practice is plasma spray process [1,2]. This is due to certain advantages such as simplicity, high deposition rates, variable coating porosity, variable phase and structure. However, due to the extremely high temperature of the plasma flame and the rapid cooling rate, the composition and the structure of the HA coatings are greatly changed from those of the original powders. HA powder may be melted, with some of the melt becoming amorphous calcium phosphate or becoming dehydroxylated or decomposed during spray process [1,2,3,4].The purpose of this study is to evaluate and characterize the coating of injection moulded Cobalt based metallic femoral hip stem produced by metal injection moulding (MIM) technique.

The popular technique of the HA coating deposition that is used in the industrial practice is plasma spray process [5,6,7,8]. This is due to certain advantages such as simplicity, high deposition rates, variable coating porosity, variable phase and structure. However, due to the extremely high temperature of the plasma flame and the rapid cooling rate, the composition and the structure of the HA coatings are greatly changed from those of the original powders. HA powder may be melted, with some of the melt becoming amorphous calcium phosphate or becoming dehydroxylated or decomposed during spray process [3,4,9,10].

In this study, the commercial HA powders were used as the feedstock. The phase composition of coatings was analyzed by the use of X-ray diffraction method. The homogeinity of the deposit and coating thickness were evaluated using scanning electron microscope (SEM).

2. MATERIALS AND METHOD

2.1 Fabrication of the Hip Stem

The hip stem produced using MIM technique and has been discussed elsewhere [11,12]. The 90 %-22 µm F75 Co-Cr-Mo powder used in the present study was obtained from Sandvik, UK. The mean particle size distribution was determined using HELOS Particle Size Analysis WINDOX 5 and around 15 micron. A scanning electron micrograph showing the powder morphology is indicated is Figure 1.The powder was mixed with a natural polymer based binder (palm stearin) at a solid loading of 65-volume % for injection molding. The binder system consists of 70-weight % of palm stearin and remaining 30-weight % of polyethylene, which represent the remaining 35-volume %. Mixture of powder and binder were dry mix followed by the entry into the Z-Blade mixer heated to 160°C. The mixing was left for 1 ½ hour. After mixing has completed, the heater was shut off and the feedstock was allowed to cool with the mixing blade still in motion. This procedure gives a granulated feedstock.

The granulated feedstock then injected into hip stem using a simple, vertically aligned and pneumatically operated plunger machine, MCP HEK-GMBH. Test bars were successfully molded at temperature of 200oC at pressure 300 bar. The test bars were debound by a two-step process where at the first stage the samples were solvent debound in order to removed all the wax portion of the binder, in this case palm stearin which is consist the major fraction of the binder. Molded samples termed the green body were arranged in a glass container, which then immersed in heptane and held at temperature 60°C for 5 hours. The glass container was covered to prevent evaporation of the heptane during extraction Subsequent thermal pyrolysis was performed in Lynn Furnace. The thermal debinding cycle consisted of 1°C/min to 450°C and soaking for 1 hour before furnace cool. Sample that completely undergoes thermal debinding termed the brown body.The components were sintered in vacuum furnace with the heating rate at 10°C/min to the sintering temperature of 1390°C, and held for 1 hour at this temperature before cooled down by furnace cool.

2.2Plasma Spray Coating Process

The feedstock were HA powder (Captal 60) supplied by Plasma Biotal Ltd UK. The particle size distribution of the powder was determined by Laser particle size analyser. The substrate of femoral hip stem used is injection moulded CoCrMo alloy powder. Its surface was grit blasted with alumina in order to roughen the surface. The substrate was then ultrasonically cleaned with ethanol for 15 minutes The HA coating process was produced using Praxair Plasma spray system with model SG-100 plasma spray torch as shown in Figure 1. The spraying parameters used for the spraying is shown in Table 1

Figure 1 Praxair Plasma spray system with model SG-100 plasma spray torch

The HA powder was injected into a very high temperature plasma flame that was formed by ionising the gaseous (argon and helium), where it is rapidly heated and accelerated to a high velocity and impacted on the substrate, rapidly cooled and finally formed coatings. The HA coatings was evaluated using X-ray diffraction to determine the phase present. The SEM analysis was carried out on the surface of the coating and the cross sectional in order to identify the microstructure evolution of the sprayed HA.

Table 1: Parameter for plasma spray HA

Sample	Set B1	Set B2
Current (setting value) (amp)	500	800
Voltage (actual value) (v)	30.2	30.2
Primary gas (psi)	50	50
Secondary gas (psi)	60	60
Carrier gas (psi)	30	30
Spraying distance (mm)	80	80
Torch speed (mm/s)	300	300
Preheat passes	2	2
Spraying pasess	3	3

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3. RESULTS AND DISCUSSIONS

3.1 Fabrication of the Hip Stem

A sintering temperature of 1390°C was chosen for densification of the test bar in vacuum atmosphere. Pores are eliminated as part of particle bonding during high-temperature sintering [5]. Sintering densification normally take place close to the me melting temperature of the material, where the bonds of the particles are bonding together by the atomic motion of the individual atoms via either solid state or liquid phase. As the temperature arises, the atomic motion occurs faster. Likewise, sintering temperature differs for each material.

This powder is usually sintered slightly above its solidus temperature; however, the solidus temperature varies depending on composition, especially carbon content [11]. Sintered sample properties are shown in Table 1. The high packing density of the F75 powder resulted in high final density that is 8.20 g/cm3. As can be seen, the samples average density is almost the same as ASTM F75 density, which is 8.28 g/cm3 with the elongation of 10%. The detail sintered density and tensile strength at different sintering temperature as in Figure 1. For plasma spray process, the hip stem sintered at 1390°C has been chosen for further study.

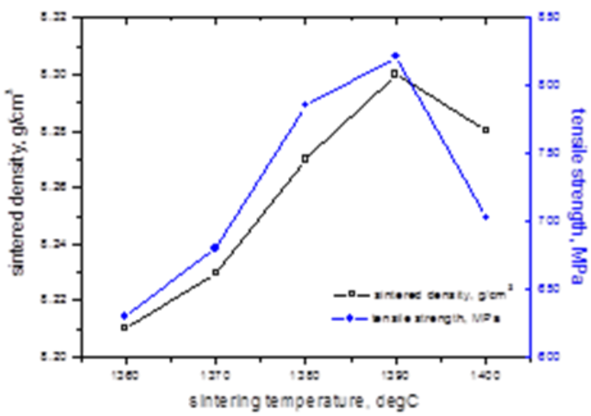


Figure 2: The sintered densities and tensile strength of the hip stem at different sintering temperatures.

3.2 HA Powder Characterization.

Figure 2 shows an XRD spectrum obtained from HA powders. The HA powders are fully crystalline phase as indicated by very sharp peak. All the peak matched with the reference with 100% crystallinity. The high intensities observed could be due to the HA crystals having the same particle orientation.

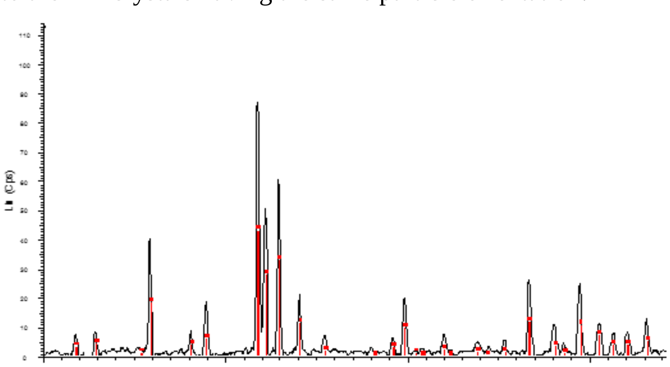


Figure. 2: X-ray diffraction pattern of HA precursor powder before plasma spraying

The SEM morphology of the HA powders is shown in Figure 3. The HA particles are quite spherical while each particle agglomerated by many fine particles with the HA powder particles were porous. The particle size distribution of the HA powders was found mainly within 10 to 100 um with the mean at around 60 um

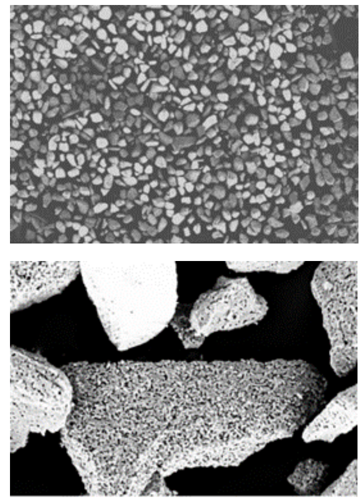


Figure 3: The SEM micrographs show the HA starting powder at different magnification

3.3 CoCrMo substrate surface of hip stem

Abraded metallic surface have been reported to be able to aid the adhesion of plasma sprayed HA particles since the rough surface will strengthen the coating adherence to the metallic hip stem. Grit blasting and ultrasonic cleaning under acetone will also not only clean the surface of any impurities, but also de-grease it. This technique is crucial because impurities or grease present on the stainless steel surface will greatly affect the coating adhesion and thickness. Figure 4 shows rough surface of hip stem after grit blasting.

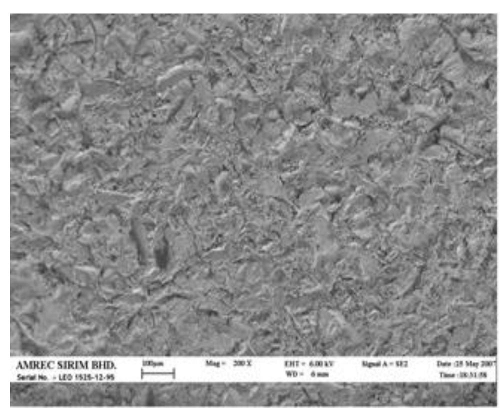
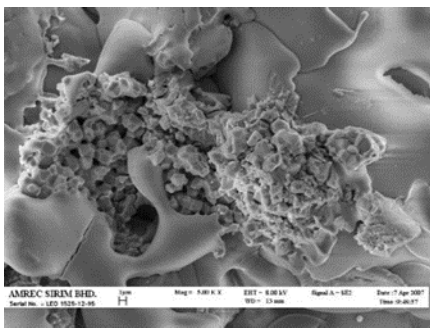


Figure 4: SEM of rough surface of hip stem after grit blasting process will strengthen the coating adherence to the metal substract

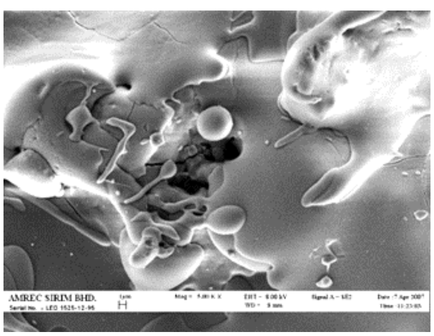
Figure 5: The final product, uncoated and coated with HA powder

3.4 Surface Morphology of Coated Surface

Surface morphology of the coatings are shown in Fig.6a (B1) and b (B2). Parameters of coating for B1 and B2 as in Table 1.



a) B1 (500amp)



b) B2 (800 amp)

Figure. 6: SEM micrographs showing surface morphology of B1 and B2 HA coatings

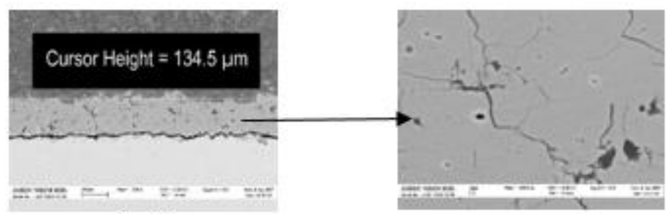
For the B1, the morphology of the coating was dominated by unmelted and partially melted particles over a small amount of flattened splats. These particles are quite large with a partially melted skin or have been crushed into fine particles that spread on the splats. A coating can be seen to have rough surface morphology with many visible cracks. As the coating cools down the cracks observed in the coating are most likely due to the relief of differential thermal stress.

Despite the remains of some partially melted particles, the morphology of coating for Fig. 6b was mainly composed of phases including the spheroidised particles, accumulated splats and flatten splats. B2 micrograph exhibited enhanced particle melting and spreading due to the higher plasma temperature. In addition, some pores but no microcracks were observed on the surface of the coating

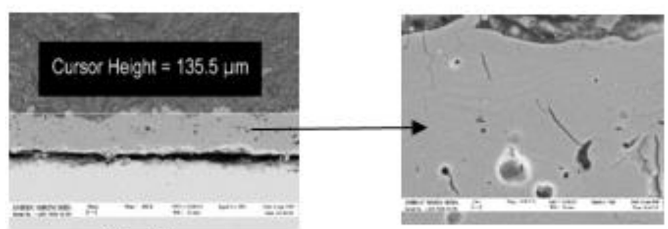
3.5 Cross Sectional Morphology

The cross sectional microstructure of the coatings are shown in Figure 7. For set B1 and B2, the lamellar structure can be identified and a large amount of pores were distributed through the coating matrix. The coating thickness of the B1 is 134.5 μm and for B2 is 135.5 um respectively. There are also small cracks at interface and within the cross-section coating samples indicates a bad adhesive strength between coating and substrate.

Many microcracks were observed, mostly perpendicular to the coating-substrate interface, indicating high tensile stress along the coating–substrate interface direction in the coating during the cooling. These microcracks were produced during either the spraying or sample polishing preparation especially for B1 sample.



a) B1



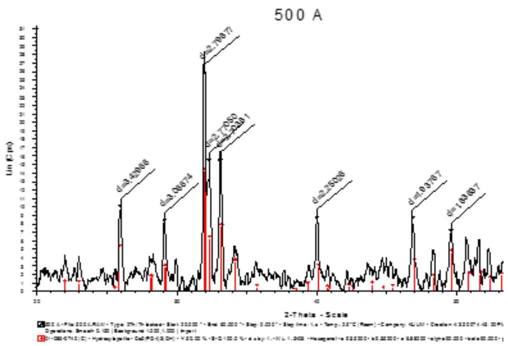
b) B2

Figure 7: SEM micrographs show a cross sectional area of plasma sprayed HA coating, a) B1 sample and b) B2 sample

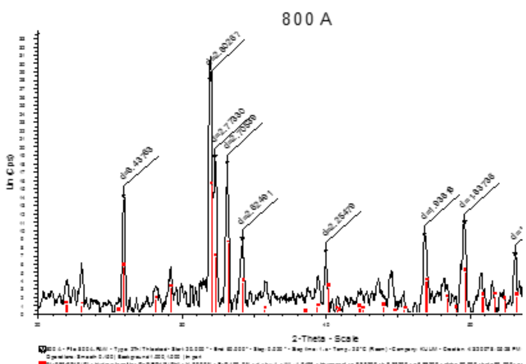
The particles/droplets may be subjected to high densification due to the high flame temperature and low surface tension, and subsequent compaction and coalescence upon striking onto substrate during spraying process; thus the thermal spray coating usually exhibits a lamellar structure. [2]

3.6 XRD Results

Figure 8a and b shows the XRD results of the coatings. The effect of the spraying parameters exhibited some differences on the XRD pattern of the HA coatings as compared to the initial XRD pattern of the HA powders. It was found that the overall intensity peaks of the HA coatings were reduced and the crystalline phases was decreased, while the amorphous hump is slightly obvious. This indicated that the HA coatings structure was altered from those of the original powder after undergone a very high temperature plasma stream and rapid cooling. To gain a better understanding of the phases changes during the HA coatings, further systematic studies of the various parameters can be suggested



a) B1



b) B2

Figure 8: The x-ray diffraction pattern of plasma sprayed HA coating indicating the mixture of crystalline and amorphous phases within the coating

4. CONCLUSIONS

The current work has concentrated on the fabrication of the hip stem using metal injection moulding process. The mechanical properties of the final products complied with the ASTM F75. HA plasma spray coating was used to coat the hip stem using two spray current. This focus is important because many parameters are incorporated during the spray process. The parameters used have shown the effects of the coating, which has been observed by SEM and XRD. Phases and structure of the HA coatings varied with respect to the spray parameters. Surface morphology and the cross sectional microstructure of the higher current reveals enhanced particle melting and spreading, lower porosity and reduce microcracks. Further study need to done for optimized the coating layer.

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