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Hydroxyapatite/silica Nanopowders Deposition on Ti Substrate by Plasma Spray Method

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ABSTRACT

In this work, hydroxyapatite/silica nanopowders were granulated to fabricate plasma sprayable feedstocks. For this purpose, the wet powders obtained by heating a hydroxyapatite/silica slurry, were stirred and sieved. To realize the feedstock application in the plasma spray process, powders were deposited on the titanium substrate. The morphology of granulated feedstock and sprayed coating were studied by using field emission scanning electron microscopy (FESEM). The evaluation of properties of sprayable powder such as apparent density and flow rate of feedstock was performed according to ASTM Nos. B 212-99 and B 213-03 standards. The results demonstrated that the granules were spherical and semi-spherical in shapes. The apparent density and flow rate of granulated feedstock were 540 kg/m^3 and 0.1089 g/sec, respectively. Also, the granules yielded the coating with molten/unmolten regions and porosity.

1. INTRODUCTION

The chemical, structural and biological properties of Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HA) is similar to human bone. Therefore, it is widely used as a coating on metal implants [1-4]. In the recent years, many attempts have done to improve hydroxyapatite coating properties (e.g. mechanical and biological properties) and different materials have added to produce composites such as metal particles, bioglasses, ceramics (alumina, titania, zirconia, silica, etc.) [1, 5-7]. Ganjali et al. used laser-induced liquid deposition (LLD) technique to deposit bioactive nanocrystalline HA films on the titanium substrates at the room temperature under the various exposure times. The results showed well crystalline HA coating that was prepared and the crystallite size had been increased and the morphology had been changed from rod to mass shape by increasing the laser irradiation time. Also, the corrosion behavior of the coating was evaluated in the simulated body fluid (SBF). The results showed that, the corrosion resistance of the coated substrates had been improved by choosing the appropriate exposure time [8].
Plasma spray is one of the most commercially techniques to deposit hydroxyapatite (HA) on the metal implants [9]. Generally, powders with size ranging from 10 to 100 μm are used in conventional thermal spray processes [10]. Nanoparticles should be granulated in the plasma spray technique. One of the reasons for nanopowder granulations is their poor flowability [11]. Nanomaterials clog their route in the plasma spray device. Nanoparticles are too light for plasma spraying [12] and they cannot be carried by gas flow, so their deposition is inefficient [13].
Dadfar et al. had been plasma sprayed YSZ powders in the water with various parameters and it resulted in spherodizing of particles and improving the properties of the resulting powders [14]. In the another research, granulated glass powder had been plasma sprayed to produce phlogopite (MACOR) glass-ceramic coating. The coating showed chemical stability and there was no reaction with Fe [15].
There are many industrial techniques to granulate ceramic powders. Some of them are atomizing, fusing, spray drying, plasma spheroidizing, sol-gel method, etc. [16]. In some granulation methods, the organic binders are used to cling the ceramic particles together [17]. Interaction between binders and particles are considerable. In aqueous solutions at pH 2-3, silica surface covered with an adequate poly (vinylalcohol) (PVA). Additional PVA causes no coagulation. In natural and basic solutions, cetyltrimethyl ammonium bromide (CTAB) should be adsorbed before PVA [18]. Poly (vinylbutyral) (PVB) is the production of PVA and butyl aldehyde reaction in the presence of an acid

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catalyst [19]. It has good compatibility with inorganic materials. Generally, PVB is used to produce organic-inorganic hybrid composites [20].

Also, the properties of materials are important to use in the granulation method [16]. HA is slightly soluble in distilled water; insoluble in alkaline and soluble in acidic solutions [21]. The solubility of amorphous silica in water is about 100 ppm at 25 ºC, in which silicic acid is produced. Its solubility is about 400 ppm at 80 ºC. Polymerization takes place in supersaturated solutions of silicic acid in pure water,. The solubility of amorphous silica in ethanol is 164 ppm at 500 ºC [18].

In this study, nano HA powders were synthesized by using the sonochemical method. Then nano HA/silica powder were granulated to produce plasma sprayable feedstock. FESEM analysis, X-ray diffraction (XRD), apparent density and flow rate evaluations were carried out to characterize the feedstocks. Then the feedstocks were plasma sprayed on the titanium substrate and coated with molten/unmolten region and porosity, which makes it more suitable for cell growth.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

A Nano HA powders were synthesized by using the sonochemical method [22]. For this purpose, 50 mmol of diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) in 50 ml distilled water and 84 mmol hydrated calcium nitrate ($Ca(NO_3)_2.4H_2O$) in 50 ml absolute ethanol were prepared. Then, the first solution added dropwise to another one at pH ≥ 10 for 1 hr in the probe sonicator (Misonix S400, Ti horn, 20 KH, 500 W/cm^2, USA). To complete reactions, the sonication process was continued for 30 minutes. Ammonium solution was used for controlling the pH. The power of the sonicator was set at 50 W, while the temperature of experiment was kept below 30 ºC. Resulting precipitates were centrifuged and washed by absolute ethanol three times. Then, it collected, dried at 80 ºC for 5 hr and crushed by a laboratory mortar and pestle for obtaining the fine powder. The powder was finally calcined at 300 ºC for 1 hr. All the chemicals were analytical grades of the Merck chemical company.

Nano amorphous silica powder (US nano research, Stock No. US3438, CAS# 7631-86-9) with an average particle size of 20-30 nm, PVB powder (ACROS) and titanium (Grade 2) were commercially obtained in this study.

2.2. Fabricating of feedstocks (granulation)

The powder with 95 wt.% nano HA and 5 wt.% nano amorphous silica were mixed in absolute ethanol and ultrasonically dispersed to obtain a homogenous mixture. The PVB solution of 3 wt.% (in absolute ethanol) was added to the mixture and ultrasonic dispersion was continued. The mixture was heated at 60-70 ºC and stirred by using an overhead stirrer until much of the absolute ethanol was vaporized and a wet solid bulk was obtained. The wet solid bulk was crushed to obtain wet powders and then it stirred by using overhead stirrer. The powder was sieved and 37-75 µm powder was separated. The out-of-size powders could be wetted with the little amount of the absolute ethanol and the prepared powders were mixed, crushed, stirred and sieved again.

2.3. Atmospheric plasma spray deposition

The feedstocks were plasma sprayed on the titanium substrate (10*10*4 mm) by using 3MB METCO gun and different spraying parameters mentioned in Table 1. Prior to plasma spraying, sand blasting on the substrate surface was applied that resulted in roughness average of 3.5 µm.

TABLE 1. Plasma spray parameters used to HA/Silica deposition on the titanium substrate

Spraying parameter	Value
Arc current	400 A
Arc voltage	55 V
Primary gas (argon) flow rate	80 SCFH
Secondary gas (hydrogen) flow rate	15 SCFH
Spray distance	80 mm

2.4. Characterization

XRD of nano HA and nano amorphous silica powders were performed by using aSiemens D500 device with Cu kα radiation (λ=1.54 Å) at 30 kV and 250 mA. All samples were examined in the 2θ range from 10º to 80º with the scanning speed of 2 2θ minute^{-1}, a step size of 0.02º and the step time of 0.5 sec.

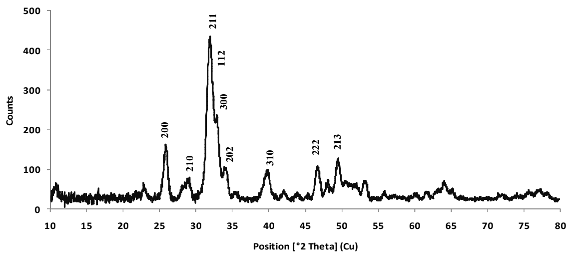
The FESEM and energy dispersive X-ray spectroscopy (EDS) analysis of HA, granulated powders and coating were performed at 15 KV (MIRA3, TESCAN, Czech Republic). The evaluation of apparent density and flow rate of feedstocks were performed according to ASTM Nos. B 212-99 and B 213-03 (by using the Hall Flowmeter Funnel).

3. RESULTS AND DISCUSSION

Fig. 1a shows the XRD pattern of synthesized HA. By checking the related patterns of the X'Pert program, it was confirmed that the HA pattern is in accordance with JCPDS card, HA, 00-001-1008. The FESEM image of the HA powder is shown in Fig. 1b. It shows that the size of the HA particles are approximately in the range of 20-40 nm. Also, it shows the tendency of the powders to agglomeration.

The FESEM images of the feedstocks are shown in Fig. 2.

(a)



(b)

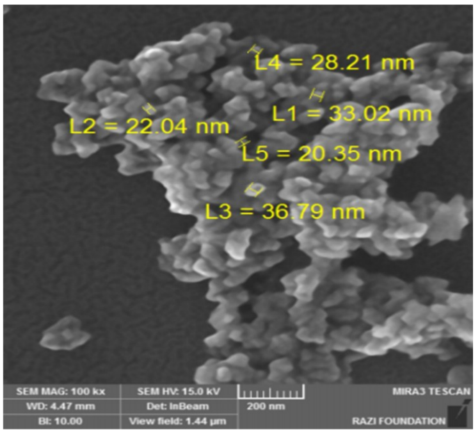


Figure 1. (a) XRD pattern and (b) FESEM image of synthesized hydroxyapatite

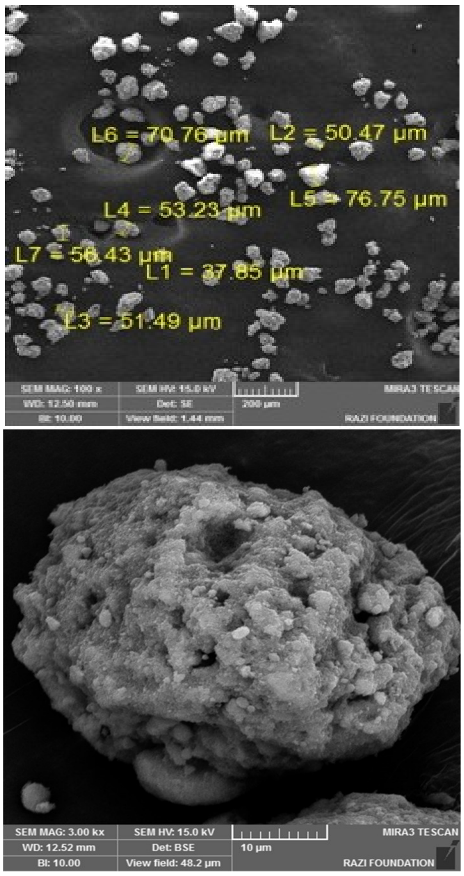


Figure 2. FESEM images of HA/silica feedstocks

It is confirmed that the size of feedstocks are in the range of 37-75 μm by using imageJ software. Also, the powder includes spherical and semi-spherical with some angular particles. The EDS results of feedstocks are shown in Fig. 3 and Table 2. The results are confirmed the presence of Ca, P and Si in the feedstocks.

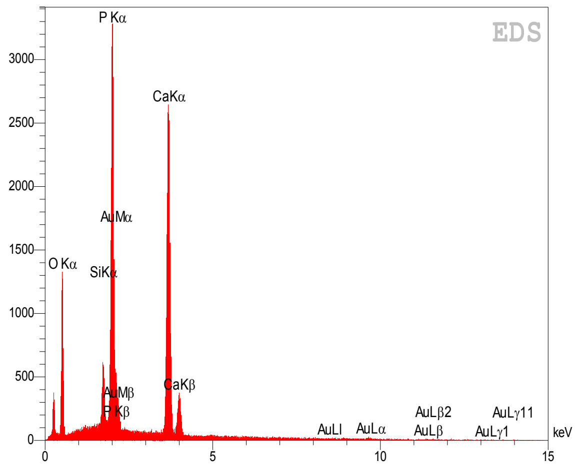


Figure 3. The EDS analysis of HA/silica feedstocks

Apparent specific mass of feedstocks were determined to 540 kg/m^3. It was reported that the apparent specific mass of the agglomerates resulted from spray drying process of atmospheric plasma spray could range from less than 1000 kg/m^3 to 2000 kg/m^3 [11]. The feedstocks mass flow rate was 0.1089 g/sec.

Fig. 4 shows FESEM image of successfully plasma sprayed feedstocks on the titanium substrate. The image showed the molten region with unmolten powders and porosity in the coating as a result of the molten/semi-molten feedstocks in the plasma spray process. The presence of porosity causes better osteoconduction and osteoinduction [23-24].

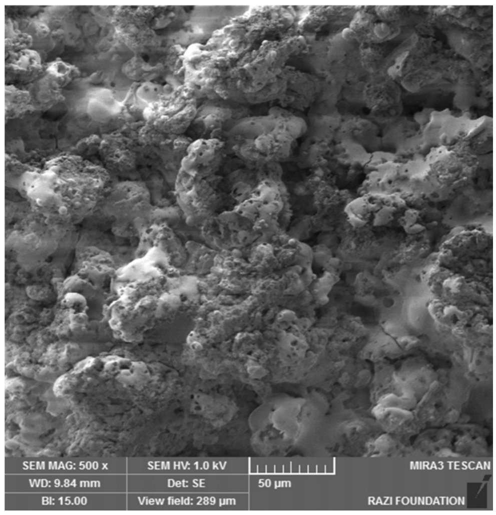


Figure 4. FESEM image of deposited feedstocks on the titanium substrate via plasma spray process

4. CONCLUSION

For fabricating the plasma sprayable feedstocks, the nano size HA/Silica powders were granulated via the procedure described in this article. The feedstocks were spherical and semi-spherical in shape with some angular particles. These feedstocks with apparent density and flow rate of 540 kg/m^3 and 0.1089 g/sec were successfully plasma sprayed on the titanium substrate by using parameters mentioned in this article and made a coating with molten/unmolten region and porosity. This structure is due to molten/semi-molten feedstocks and makes it more suitable for cell growth.

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REFERENCES

1. Fidancevska, E., Ruseska, G., Bossert, J., Min Lin, Y., Boccaccini, A.R., "Fabrication and characterization of porous bioceramic composites based on hydroxyapatite and titania", ***Materials Chemistry and Physics***, Vol. 103, (2007), 95-100.
2. Palanivelu, R., Kumar, A.R., "Scratch and wear behaviour of plasma sprayed nano ceramics bilayer Al_2O_3-13 wt% TiO_2/ hydroxyapatite coated on medical grade titanium substrates in SBF environment", ***Science Applied Surface***, Vol. 315, (2014), 327-329.
3. Kong, D., Dan, L., Yong Zhong, W., Chao-Zheng, Z., "Mechanical properties of hydroxyapatite-zirconia coatings prepared by magnetron sputtering", ***Transformation of Nonferrous Metals Society of China***, Vol. 22, (2012), 104-110.
4. Lee, H.U., Jeong, Y.S., Park, S.Y., Jeong, S.Y., Kim, H.G., Cho, C.R., "Surface properties and cell response of fluoridated hydroxyapatite/TiO_2 coated on Ti substrate", ***Current Applied Physics***, Vol.9, (2009), 528-533.
5. Mumjitha, M., Raj, V., "Fabrication of TiO_2-SiO_2 bioceramic coatings on Ti alloy and its synergetic effect on biocompatibility and corrosion resistance", ***Journal of the Mechanical Behavior of Biomedical Materials***, Vol. 46, (2015), 205-221.
6. Morks, M.F., "Fabrication and characterization of plasma-sprayed HA/SiO_2 coatings for biomedical application", ***Journal of the Mechanical Behavior of Biomedical Material,*** Vol. 1, (2008), 105-111.
7. Singh, G., Singh, H., Sidhu, B.S., "Characterization and corrosion resistance of plasma sprayed HA and HA–SiO_2 coatings on Ti–6Al–4V", ***Surface & Coatings Technology***, Vol. 228, (2013), 242–247.
8. Ganjali, M., Pourhashem, S., Vaezi, M.R., "Characterization and corrosion behavior of hydroxyapatite- coated titanium substrates prepared through laser induced liquid deposition technique", ***Advanced Ceramics Progress***, Vol. 1, No, 3, (2015), 28-33.
9. Singha, G., Singh, H., Sidhu, B.S., "Corrosion behavior of plasma sprayed hydroxyapatite and hydroxyapatite-silicon oxide coatings on AISI 304 for biomedical application", ***Applied Surface Science***, Vol. 284, (2013), 811-818.
10. Salimi Jazi, H., Advanced plasma spray applications, 1st ed. UK: IntechOpen;(2012).
11. Loghman-Estarki, M.R., Edris, H., Shojarazavi, R., Jamali, H., Ghasemi, R., Pourbafrany, M., Erfanmanesh, M., Ramezani, M., "Spray drying of nanometric SYSZ powders to obtain plasma sprayable nanostructured granules", ***Ceramics International***, Vol. 39, (2013), 9447-9457.
12. Lin, X., Zeng, Y., Zhou, X., Ding, C., "Microstructure of alumina-3 wt% titania coatings by plasma spraying with nanostructured powders", ***Materials Science and Engineering A***, Vol. 357, (2003), 228-234.
13. Lima, R.S., Marple, B.R., "Thermal spray coatings engineered from nanostructured ceramic agglomerated powders for structural, thermal barrier and biomedical applications: A review", ***Journal of Thermal Spray Technology***, Vol. 16, No. 1, (2007), 40-63.
14. Dadfar, M.R., Rahimipour, M.R., Vaezi, M.R., Gholamzadeh, A., "Characterization and phase transformation of spherical YSZ powders fabricated via air plasma spray method", ***Advanced Ceramics Progress***, Vol. 2, No. 4, (2015), 32-38.
15. Faeghinia, A., Shahgholi, N., Jabbari, E., "Phlogopite glass-ceramic coatings on stainless steel substrate by plasma spray", ***Advanced Ceramics Progress***, Vol. 2, No. 2, (2016), 16-21.
16. Padmanabhan, P.V.A., Ramanathan, S., Sreekumar, K.P., Satpute, R.U., Kutty, T.R.G., Gonal, M.R., Gantayet, L.M., "Synthesis of thermal spray grade yttrium oxide powder and its application for plasma spray deposition", ***Materials Chemistry and Physics***, Vol. 106, (2007), 416-421.
17. Shen, F., Lu, X., Bian, X., Shi, L., "Preparation and hydrophilicity study of poly(vinyl butyral)-based ultrafiltration membranes", ***Journal of Membrane Science***, Vol. 265, (2005), 74-84.
18. Iler, R.K., The chemistry of silica: Solubility, polymerization, colloid and surface properties, and biochemistry, 1st ed. New York: John Wiley; (1979).
19. Cao, X.Q., Vassen, R., Schwartz, S., Jungen, W., Tietz, F., Stoever, D., "Spray-drying of ceramics for plasma-spray coating", ***Journal of the European Ceramic Society***, Vol. 20, (2000), 2433-2439.
20. Obradovic, V., Stojanovic, D.B., Kojovic, A., Zivcovic, I., Radojevic, V., Uskokovic, P.S., Alecsic, R., "Electrospun poly(vinylbutyral)/silica composite fibres for impregnation of aramid fabrics", ***Material Plastic***, Vol. 51, No. 3, (2014), 319-322.
21. Park, J., Bioceramics Properties, Characterizations, and Applications, 1st ed. New York: Springer-Verlag; (2008).
22. Barandehfard, F., Keyanpour-Rad, M., Hosseinnia, A., Kazemzadeh, S.M., Vaezi, M.R., Hassanjani-Roshan, A., "Sonochemical synthesis of hydroxyapatite and fluoroapatitenanosized bioceramics", ***Journal of Ceramic Processing Research***, Vol. 13, No. 4, (2012), 437-440.
23. Kokubo, T., Bioceramics and their clinical applications, 1st ed. Cambridge: Woodhead Publishing; (2008).
24. Farrokhi-Rad, M., Loghmani, S.K., Shahrabi, T., Khanmohammadi, S., "Electrophoretic deposition of hydroxyapatite nanostructured coatings with controlled porosity", ***Journal of European Ceramic Society***, Vol. 34, (2014), 97-106.