Heat treatment of plasma sprayed tricalcium phosphate coatings deposited on substrate Ti-6Al-4V ELI

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ABSTRACT

Micron-sized spray-dried tricalcium phosphate (TCP) powder has been deposited successfully on the substrate of Ti-6Al-4V ELI alloy through an atmospheric plasma spraying process. Further, heat treatment of the deposited coating is carried out at a temperature of 600 °C for the holding time duration of 2 h in a muffle furnace. Phase identification of the as-deposited and post heat-treated TCP coatings is analyzed through an X-ray diffractometer (XRD). The top morphology and microstructure of both coatings are examined with the help of the field emission scanning electron microscope (FESEM). The porosity and micro-crack are found to be reduced by heat treatment. Fully molten particles are noticed to be dominant on the top surface of the coating obtained after performing heat treatment. The transformation of secondary phases, namely tetra calcium phosphate (TTCP) and calcium oxide, into stable tricalcium phosphate is achieved by heat treatment.

1. Introduction

Tricalcium phosphate (TCP) and hydroxyapatite are two well-known bio-ceramic members of the calcium phosphate family (Hussain & Sabiruddin, 2021a, 2021b). Over many years, different deposition techniques have been employed to coat calcium phosphate-based ceramics powder as coatings on metal substrate surfaces in the fields of biomedical applications. The atmospheric plasma spray (Hussain et al., 2023; Morks, 2008), sol-gel deposition (Jafari et al., 2016), sputtering deposition (Surmeneva et al., 2015) composition and morphology of a radio-frequency (RF, electrodeposition (Pei et al., 2019), pulsed laser deposition (Nelea et al., 2000), electrophoretic deposition (Farnoush et al., 2015), cold spray (Chen et al., 2018), spin coating (Yuan et al., 2016), warm spray (Yao et al., 2018), ion beam assisted deposition (Bai et al., 2010), suspension spray (Xu et al., 2016), and thermal spray deposition (Gligorijević et al., 2016; Mejias et al., 2016) are the examples of such methods. Among these, thermal spray processes can offer very high flame temperatures to melt the ceramic powder and deposit a thick coating. The thermal and kinetic energy of the depositing droplets decides the properties of the final coating (Vahabzadeh et al., 2015). In the thermal spray group, atmospheric plasma spraying (APS) is considered to be the most versatile method for developing calcium phosphate coatings. The US Food and Drug Administration (FDA) recommended and approved the APS method for biomedical applications in view of the safety factors.

One of the potential ways to improve the characteristics of the calcium phosphate coating is to conduct heat treatment on it. Li et al. (2002) carried out the heat treatment on the calcium phosphate coatings fabricated by the technique of high-velocity oxy-fuel (HVOF) and studied the role of the heat treatment process on the characteristics of the fabricated coatings. However, the influence of heat treatment on the microstructure and phases of plasma-sprayed tricalcium phosphate coating is rarely studied.

In this study, tricalcium phosphate (TCP) coating is initially deposited by the APS process on the substrate of Ti-6Al-4V alloy. Then, the influence of the heat treatment process on the characteristics of the developed coating is studied through different characterization techniques such as

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image analysis (Image J) software, X-ray diffraction, and FESEM.

2. Materials and Methods

The commercial sub-micron-sized TCP powder is procured and agglomerated by spray drying technique to improve its flowability. The ultrasonic cleaner is used to remove grease, dust, and other loose contaminants from the surface of the substrate Ti-6Al-4V ELI (extra low interstitial). After drying, the substrates are grit blasted in a suction-type blast cabinet to obtain average surface roughness of around 5 µm (Hussain et al., 2022). Loosely adhered particles are removed from the grit-blasted surface by an air jet. Before starting the coating operation, the substrates are pre-heat treated up to a temperature of 200 ℃ through the APS gun to improve the wettability of the surface and reduce the residual stress. APS process conditions are optimized by performing several trials to achieve better quality and adhesion of TCP coating. The optimized conditions used for the deposition of the final coating are depicted in Table 1. A 300 µm thick TCP coating is deposited on the substrate by the APS technique. Further, the TCP-coated sample is heat treated in a muffle furnace operating in a normal atmosphere. The maximum temperature and residence time are set as 600 ℃ and 2 h, respectively. Further, in the heat treatment, a heating rate of 15 ℃/min is employed and followed by furnace cooling. A slow-speed diamond cutter is used for sectioning the heat-treated and as-sprayed coatings to obtain small specimens. The specimens are then hot-mounted to polish the cross-section for microstructure study. The standard metallographic step-by-step procedure is adopted for the sample preparation. A field-emission scanning electron microscope (FESEM) is operated under secondary electron mode to investigate the cross-section microstructure and top surface morphology of the coatings. The crystalline phases observed in the as-deposited and heat-treated coatings are analyzed by the X-ray diffractometry (XRD) technique. Image J software is used to measure the porosity of both coatings by selecting the cross-section FESEM images. The portion of the image, including pores, is considered for measurement purposes. The average percentage of porosity is estimated by evaluating the area fraction of several pores present in the coating.

Table 1
Optimized process parameters for atmospheric plasma spray coatings.

Parameters	Values
Voltage (V)	45
Current (A)	790
Secondary gas (H_2) flow rate (SCFH)	6
Primary gas (Ar) flow rate (SCFH)	65
Stand of distance (mm)	100
Feed rate of powder (g/min)	10

3. Results and Discussion

The FESEM images of as-deposited plasma sprayed tricalcium phosphate coating are shown in Fig. 1-3. The top microstructure and surface morphology of the as-sprayed coating illustrated in Fig. 1 indicates the presence of both fully molten and partially melted particles on the surface. The coating is well adherent to the substrate, as shown in Fig. 2. High magnification

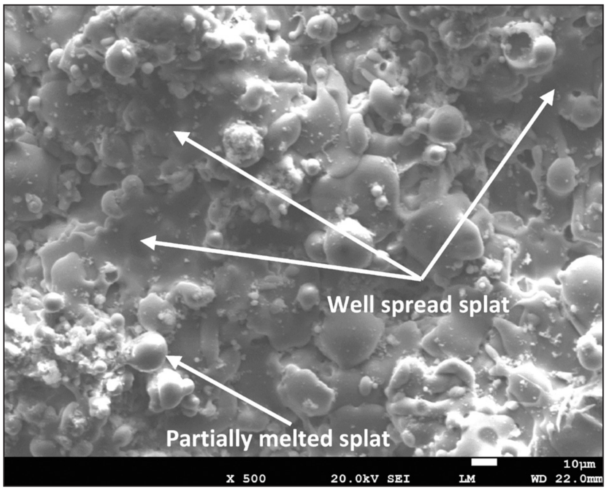

Fig. 1. FESEM image of the top surface of as-sprayed plasma sprayed tricalcium phosphate coating.

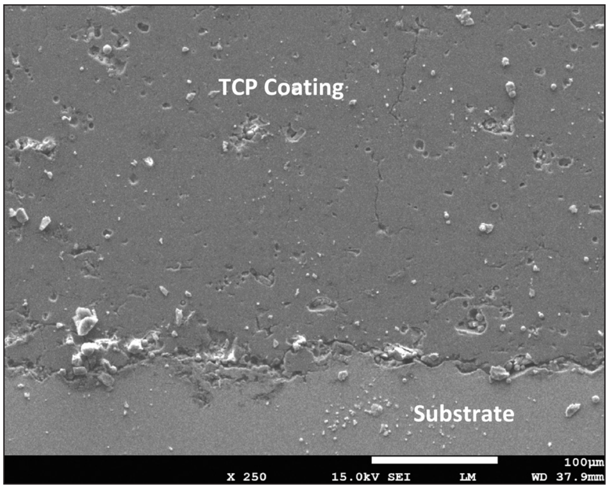

Fig. 2. FESEM image of the cross-section surface of plasma sprayed tricalcium phosphate coating.

image of the coating cross-section reveals the presence of defects, pores, and micro-cracks, as illustrated in Fig. 3. The presence of defects is due to the removal of loosely adhered un-melted TCP particles during the polishing operation. The thermal stresses caused by the cooling effects of the inhomogeneous TCP coating have resulted in the formation of cracks passing through the weak defective zones.

The FESEM images of heat-treated plasma sprayed tricalcium phosphate coating are illustrated in Fig. 4-6. The top surface morphology of the coating depicted in Fig. 4 reveals the presence of more fully melted particles as compared to the same of the as-deposited coating. The size of the partially melted globules is also appeared to be enlarged. The coating is well adherent to the substrate after post heat treatment also, as depicted in Fig. 5. From Fig. 6, the defects such as crater, pore, and micro-crack are observed to be lesser than the same of as-sprayed coating. The heating effect has caused the grains and partially melted particles to expand in volume, as clearly seen in Fig. 4. The increased volume of the grains in the solid coating has helped to suppress the pores and cracks to some extent.

The XRD characteristic patterns of the as-deposited and post heat-treated plasma-sprayed tricalcium phosphate coatings are depicted in Fig. 7. Most of the significant diffraction peaks index with the TCP phase, and few peaks belong to calcium oxide and tetra calcium phosphate in the case of as-deposited coating as depicted in Fig. 7(a). On the other hand, all the diffraction peaks are observed to be of TCP phase only for the heat-treated coating, as illustrated in

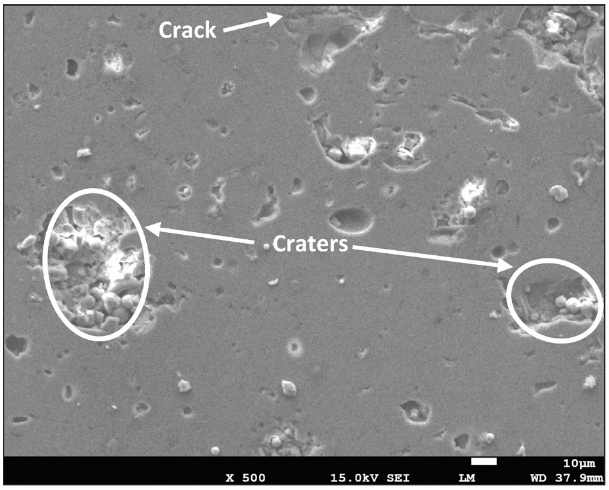

Fig. 3. High magnification cross-sectional FESEM micrograph of plasma sprayed tricalcium phosphate coating.

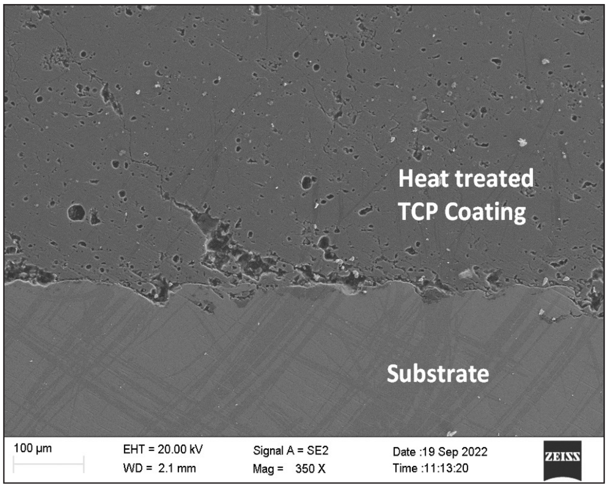

Fig. 5. Cross-sectional FESEM micrograph of the heat-treated plasma sprayed tricalcium phosphate coating.

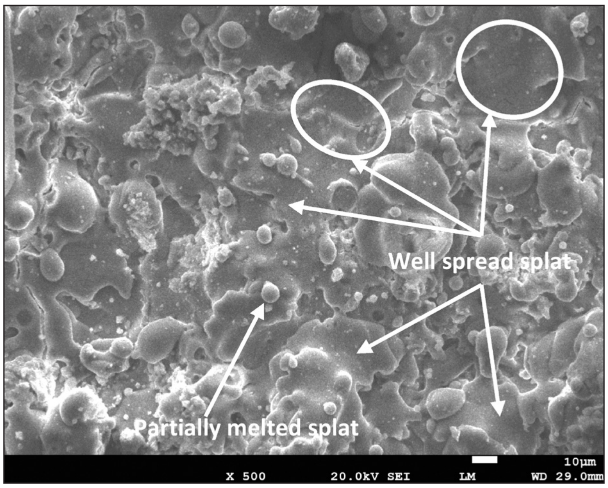

Fig. 4. FESEM micrograph of the top surface of the heat-treated plasma sprayed tricalcium phosphate coating.

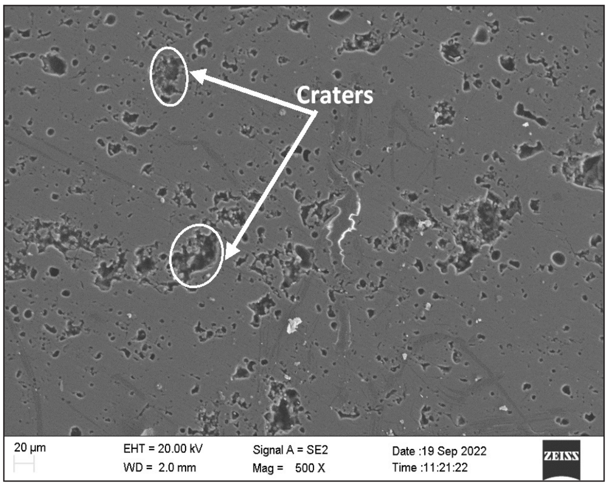

Fig. 6. High magnification cross-sectional FESEM image of the heat-treated plasma sprayed tricalcium phosphate coating.

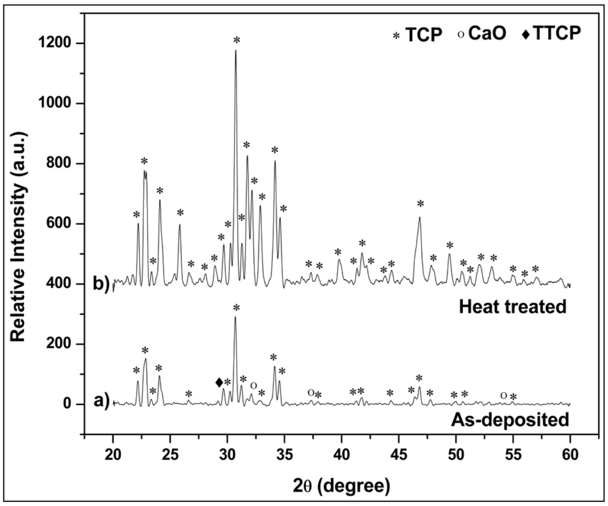

Fig. 7. XRD characteristic patterns of (a) as-deposited and (b) post heat-treated plasma sprayed tricalcium phosphate coatings.

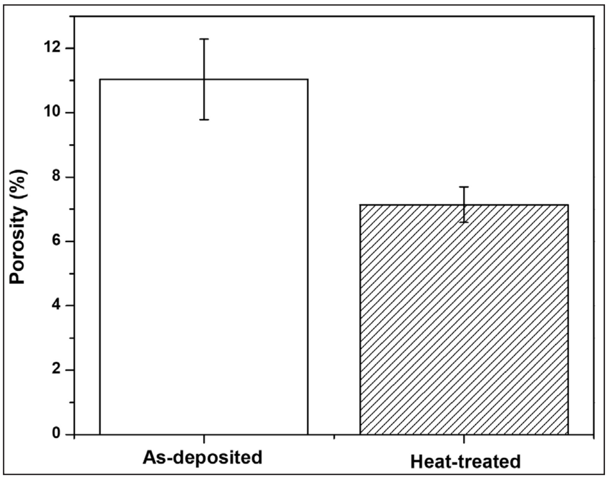

Fig. 8. Porosity percentage of as-deposited and post heat-treated plasma sprayed tricalcium phosphate coatings.

Fig. 7 (b). The peaks of the TCP phase are found to be sharper after heat treatment compared to the same of as-deposited TCP coating. This indicates increased crystallization of phases in heat-treated TCP coating. By heat treatment of the as-deposited TCP coating at 600 °C, the secondary phases, such as calcium oxide and tetra calcium phosphate, are completely transformed into stable tricalcium phosphate phases, as shown in Fig. 7(b). This is one of the major reasons for the reduction of porosity after heat treatment of TCP coating. The cell volume of the TCP phase is much more than the same of the CaO and TTCP phases. Hence, the propagation of cracks is found to be restricted in such a coated sample. The percentage of porosity estimated in the as-deposited and post heat-treated plasma-sprayed tricalcium phosphate coatings is shown in Fig. 8. Porosity percentage is found to be decreased from 11 to 7 % after heat treatment.

4. Conclusions

In the present research work, TCP coating is successfully deposited by the APS process on the titanium alloy substrate. Further, the deposited coating is heat treated at 600°C for a residence time of 2 h. The role of the post heat treatment on the coating properties, such as the morphology, phases, and microstructure, is investigated. Based on the results obtained from this study, the following important conclusions are drawn in a point-wise manner.

1. The CaO and TTCP phases formed in the as-sprayed coating can be completely converted into TCP phases by heat treatment.
2. Heat treatment helps to improve the coating density by reducing the porosity. The expansion of the partially melted TCP globules present on the top surface under the heating effect seems to improve the wettability.
3. Defects such as micro-crack and craters are observed to be lesser in post heat-treated coating than in the as-sprayed coating.

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References

Bai, X., More, K., Rouleau, C. M., & Rabiei, A. (2010). Functionally graded hydroxyapatite coatings doped with antibacterial components. *Acta Biomaterialia*, *6*(6), 2264-2273. https://doi.org/10.1016/j.actbio.2009.12.002

Chen, X., Ji, G., Bai, X., Yao, H., Chen, Q., & Zou, Y. (2018). Microstructures and Properties of Cold Spray Nanostructured HA Coatings. *Journal of Thermal Spray Technology*, *27*(8), 1344-1355. https://doi.org/10.1007/s11666-018-0776-1

Farnoush, H., Aldıç, G., & Çimenoğlu, H. (2015). Functionally graded HA–TiO2 nanostructured composite coating on Ti–6Al–4V substrate via electrophoretic deposition. *Surface and Coatings Technology*, *265*, 7-15. https://doi.org/10.1016/j.surfcoat.2015.01.069

Gligorijević, B. R., Vilotijević, M., Šćepanović, M., Vidović, D., & Radović, N. A. (2016). Surface structural heterogeneity of high power plasma-sprayed hydroxyapatite coatings. *Journal of Alloys and Compounds*, *687*, 421-430. https://doi.org/10.1016/j.jallcom.2016.06.163

Hussain, S., & Sabiruddin, K. (2021a). Synthesis of eggshell based hydroxyapatite using hydrothermal method. *IOP Conference Series: Materials Science and Engineering*, *1189*(1), 012024.https://doi.org/10.1088/1757-899x/1189/1/012024

Hussain, S., & Sabiruddin, K. (2021b). Effect of heat treatment on the synthesis of hydroxyapatite from Indian clam seashell by hydrothermal method. *Ceramics International*, *47*(21), 29660-29669. https://doi.org/10.1016/j.ceramint.2021.07.137

Hussain, S., Shah, Z. A., Sabiruddin, K., & Keshri, A. K. (2023). Characterization and tribological behaviour of Indian clam seashell-derived hydroxyapatite coating applied on titanium alloy by plasma spray technique. *Journal of the Mechanical Behavior of Biomedical Materials*, *137*, 105550. https://doi.org/10.1016/j.jmbbm.2022.105550

Hussain, S., Sharma, M., Sharma, V., Brahmane, S., & Sabiruddin, K. (2022). Effect of Ni-5Al Addition on the Properties of BaAl2O4-Based Coating Deposited with a Novel Explosive Spray Coating Technique. *Journal of Thermal Spray Technology*. https://doi.org/10.1007/s11666-022-01492-z

Jafari, H., Hessam, H., Shahri, S. M. G., Assadian, M., Shairazifard, S. H. P., & Idris, M. H. (2016). Characterizing Sintered Nano-Hydroxyapatite Sol-Gel Coating Deposited on a Biomedical Ti-Zr-Nb Alloy. *Journal of Materials Engineering and Performance*, *25*(3), 901-909. https://doi.org/10.1007/s11665-016-1944-4

Li, H., Khor, K. A., & Cheang, P. (2002). Properties of heat-treated calcium phosphate coatings deposited by high-velocity oxy-fuel (HVOF) spray. *Biomaterials*, *23*(10), 2105-2112. https://doi.org/10.1016/S0142-9612(01)00326-X

Mejias, A., Candidato, R. T., Pawłowski, L., & Chicot, D. (2016). Mechanical properties by instrumented indentation of solution precursor plasma sprayed hydroxyapatite coatings: Analysis of microstructural effect. *Surface and Coatings Technology*, *298*, 93-102. https://doi.org/10.1016/j.surfcoat.2016.04.028

Morks, M. F. (2008). Fabrication and characterization of plasma-sprayed HA / SiO2 coatings for biomedical application. *Journal of the Mechanical Behavior of Biomedical Materials*, *1*(1), 105-111. https://doi.org/10.1016/j.jmbbm.2007.04.003

Nelea, V., Ristoscu, C., Chiritescu, C., Ghica, C., Mihailescu, I. N., Pelletier, H., Mille, P., & Cornet, A. (2000). Pulsed laser deposition of hydroxyapatite thin films on Ti-5Al-2.5Fe substrates with and without buffer layers. *Applied Surface Science*, *168*(1-4), 127-131. https://doi.org/10.1016/S0169-4332(00)00616-4

Pei, L., Zhang, B., Luo, H., Wu, X., Li, G., Sheng, H., & Zhang, L. (2019). Electrodeposition of ZnO Nanoprism-Zn substituted hydroxyapatite duplex layer coating for carbon fiber. *Ceramics International*, *45*(11), 14278-14286. https://doi.org/10.1016/j.ceramint.2019.04.137

Surmeneva, M. A., Tyurin, A. I., Mukhametkaliyev, T. M., Pirozhkova, T. S., Shuvarin, I. A., Syrtanov, M. S., & Surmenev, R. A. (2015). Enhancement of the mechanical properties of AZ31 magnesium alloy via nanostructured hydroxyapatite thin films fabricated via radio-frequency magnetron sputtering. *Journal of the Mechanical Behavior of Biomedical Materials*, *46*, 127-136. https://doi.org/10.1016/j.jmbbm.2015.02.025

Vahabzadeh, S., Roy, M., Bandyopadhyay, A., & Bose, S. (2015). Phase stability and biological property evaluation of plasma sprayed hydroxyapatite coatings for orthopedic and dental applications. *Acta Biomaterialia*, *17*, 47-55. https://doi.org/10.1016/j.actbio.2015.01.022

Xu, H., Geng, X., Liu, G., Xiao, J., Li, D., Zhang, Y., Zhu, P., & Zhang, C. (2016). Deposition, nanostructure and phase composition of suspension plasma-sprayed hydroxyapatite coatings. *Ceramics International*, *42*(7), 8684-8690. https://doi.org/10.1016/j.ceramint.2016.02.102

Yao, H. L., Ji, G. C., Chen, Q. Y., Bai, X. B., Zou, Y. L., & Wang, H. T. (2018). Microstructures and Properties of Warm-Sprayed Carbonated Hydroxyapatite Coatings. *Journal of Thermal Spray Technology*, *27*(6), 924-937. https://doi.org/10.1007/s11666-018-0735-x

Yuan, Q., Qin, C., Wu, J., Xu, A., Zhang, Z., Liao, J., Lin, S., Ren, X., & Zhang, P. (2016). Synthesis and characterization of Cerium-doped hydroxyapatite/polylactic acid composite coatings on metal substrates. *Materials Chemistry and Physics*, *182*, 365-371. https://doi.org/10.1016/j.matchemphys.2016.07.044

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