PROPERTIES OF HYDROXYAPATITE SURFACE DEPOSITED BY PLASMA SPRAY TECHNOLOGIES

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Abstract

The surface properties of hydroxyapatite (HA) deposited on the Ti-6Al-4V substrates by plasma spraying were studied. Two different plasma spray technologies (hybrid plasma spray system (WSP-H) and conventional atmospheric plasma spray technology (APS)) and two various feedstock (suspension for WSP-H and powder for APS) were used for deposition of HA layers potentially suitable for bio-applications. The layers properties (thickness, chemical and phase composition) and coating-substrate interface quality were analyzed. The XRD analysis showed formation of small amount of new phases (TTCP and CaO) in layers deposited by WSP-H. Better coating-substrate interface quality of samples prepared by WSP-H was observed. The results showed the deposition of HA through liquid feedstock via WSP-H as a promising route, complementing the traditional APS powder deposition in the near future.

Keywords: Hydroxyapatite, hybrid water-stabilized plasma spray, atmospheric plasma spray technology

1. INTRODUCTION

Plasma spray technologies are widely used for various applications due to their versatility. High temperature and high deposition rates allow efficient deposition of wide range of materials. The feedstock, usually in the form of powders, is melted and deposited on a substrate, where a typical lamellar microstructure is produced. Powders as feedstock are used for conventional atmospheric plasma spraying (APS) [1; 2; 3; 4]. Another option is a liquid feedstock of suspension of solid particles dispersed in a solvent (suspension plasma spraying - SPS) or solution precursor plasma spraying (SPPS) [3; 5; 6; 7]. For suspension and solution plasma spraying, torches with high enthalpy content are primarily used. One of such plasma sources is hybrid water-stabilized plasma (WSP-H) developed at Institute of Plasma Physics CAS, v.v.i. [3; 7].

WSP-H technology uses benefits of water stabilization and gas stabilization torch. First, argon plasma is generated in the cathode section (gas stabilization) and then enters the water stabilized section, where water evaporation and steam ionization substantially increase plasma enthalpy [7]. The high-enthalpy plasma provided by the WSP-H torch may be used for thermal spraying of powders as well as liquid feedstock with high feed rates [3; 7].

Hydroxyapatite ($Ca_{10}(PO4)_6(OH)_2$, HA) is widely preferred as the biomaterial due to its favorable osteoconductive and bioactive properties. HA has similar chemical composition and crystal structure as apatite in the human skeletal system, and is therefore suitable for bone implants. Despite its ideal bioactive properties, poor mechanical properties (as fracture toughness, strength and ductility) hinder the use of HA as a load bearing implant. For these reasons, the combination of bioactive HA and mechanically strong metals are a promising approach to load bearing implants. One of the suitable materials is titanium. Titanium and titanium alloys are attractive materials for biological applications for their low density, satisfactory mechanical properties, high corrosion resistance and good biocompatibility [8; 9; 10; 11].

The objective of this study was comparing properties of hydroxyapatite layers deposited by WSP-H on Ti6Al4V and stainless steel substrate and APS on stainless steel substrate.

2. EXPERIMENTAL

2.1. Preparation of hydroxyapatite

Conventional chemical precipitation was used for preparation of hydroxyapatite suspension, i.e. reaction of calcium hydroxide and phosphoric acid under controlled temperature and pH value:

$$10\ Ca(OH)_2 + 6\ H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18\ H_2O \quad (1)$$

Part of the resulting HA suspension was used for deposition by WPS-H. Next part of HA suspension was dried by spray dryer and the obtained powder was used for deposition by APS. Atomizing the suspension into a stream of heated air flowing through the spray dryer evaporation chamber resulted in the formation of globular particles. The powder purity 98.6 % by XRD was measured.

2.2. Preparation of samples by plasma spray

HA suspension was deposited by water-stabilized plasma torch WSP-H 500 (ProjectSoft HK a.s., Czech Republic). Two sets of samples on two different substrates (stainless steel AISI 304 - WSP/S-1 and WSP/S-2; Ti-6V-4Al - WSP/T-1, WSP/T-2) were prepared by WSP. First set of samples was sprayed with standard plasma torch power level (500 A), the second set was deposited using lower power level (400 A). Feed rates were 105 and 90 g / min, respectively. Suspension injection distance was 30 mm, stand-off distance was 100 mm. Interpass cooling temperature was 200 °C. Further details on spraying of suspensions with WSP-H torch are provided in [7].

HA powder was sprayed by Praxair SG-100 atmospheric plasma spraying gun. Two sets of samples on stainless steel AISI 304 substrate were prepared with different spraying conditions (APS-1 and APS-2). Specifications of spraying conditions for respective APS sets are summarized in **Table 1**.

Table 1 Spraying conditions of samples deposited by APS

Spraying parameters		APS-1	APS-2
Net power	(kW)	15	15
Flow of main gas - argon	(scfh)	100	100
Flow of auxiliary gas - helium	(scfh)	40	60
Flow of carrier gas - argon	(scfh)	30	30
Spray distance	(mm)	120	80

2.3. Analysis

Cross section of samples deposited by WSP-H and APS was analyzed by scanning electron microscopy (SEM; FEG-SEM Zeiss Ultra Plus) and quantitative chemical analyses were performed by using energy dispersive spectroscope (EDS; EDAX XL-30). Phase composition of the deposited layers was determined using XPert Pro X-ray diffractometer (Co Kα, Kβ absorption filter) equipped with XCelerator detector (PANalytical B.V.).

3. RESULTS

Figure 1 shows morphology of the HA deposited coating by WSP-H and APS. WSP-H layers exhibited heterogeneous, fine lamellar structure with partial porosity. More pronounced "columnar-like" microstructure was observed on the layer deposited on the steel substrate when compared to Ti6Al4V substrate which can be due to the different surface roughness after grit-blasting. Aside from this, no significant differences were observed for the different substrates. The lower power settings of the WSP-H system (400 A) resulted in less efficient melting of the feedstock particles, thereby increasing the content of the non-molten particles in the final coatings (cf. WSP/T-1, WSP/T-2). APS-1 coating showed relatively homogenous structure with cracks vertically passing through the HA layer to the substrate. Non-compact layer HA with poor coating-substrate interface quality in seen in APS-2 sample, suggesting inferior adhesion to the substrate. Higher surface roughness for WPS-H layers and better coating-substrate interface quality for WPS-H substrate-coating interface than APS layers was observed. The thicknesses of deposited coatings were measured and obtained data are presented in **Table 2.**

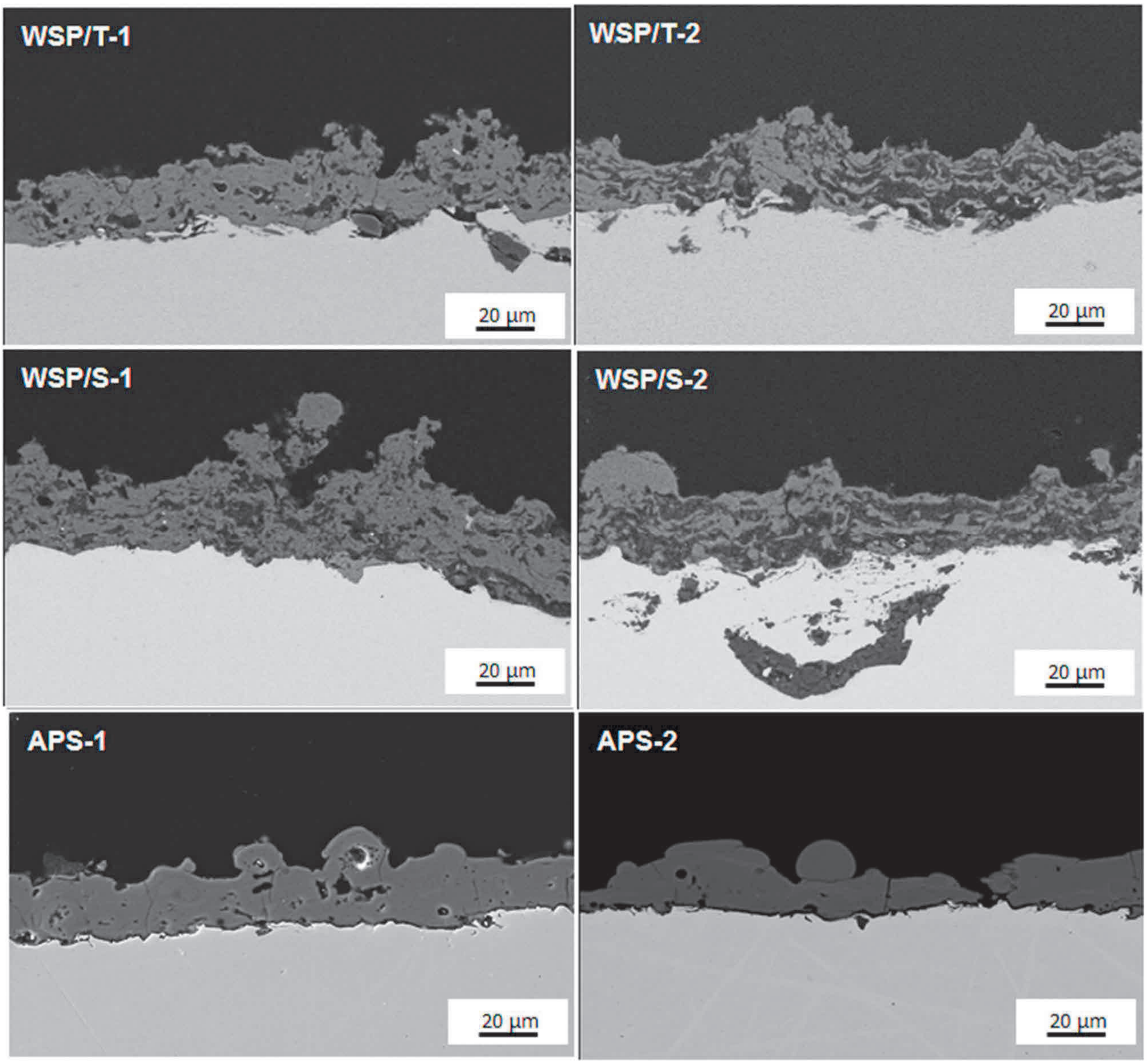

Figure 1 The structure of HA coatings produced via WSP-H and APS technologies

Table 2 Coating thickness of samples deposited by WSP-H and APS

	WSP/T-1	WSP/T-2	WSP/S-1	WSP/S-2	APS-1	APS-2
Coating thickness [µm]	31 ± 8	26 ± 9	33 ± 12	33 ± 15	24 ± 14	15 ± 10

As expected, EDS analysis showed a presence Ca, P and O in the structure for all deposited layers. The phase composition was analyzed by XRD (**Figure 2**). Less intensive transformation of HA was detected in the WSP-H layers (90 % HA, 6 % TTCP, 4 % CaO). In the case of the APS layers, substrate (Fe peaks) was detected in APS-1 layer and a large amount of HA was transformed (APS-1: 38 % HA, 44 % Ca_5P_8, 8 % CaO; APS-2: 60 % HA, 27 % CaC_2, 12 % $Ca_3(PO_4)_2$) due to increased spraying temperature and longer time, which the particles spent in the plasma jet.

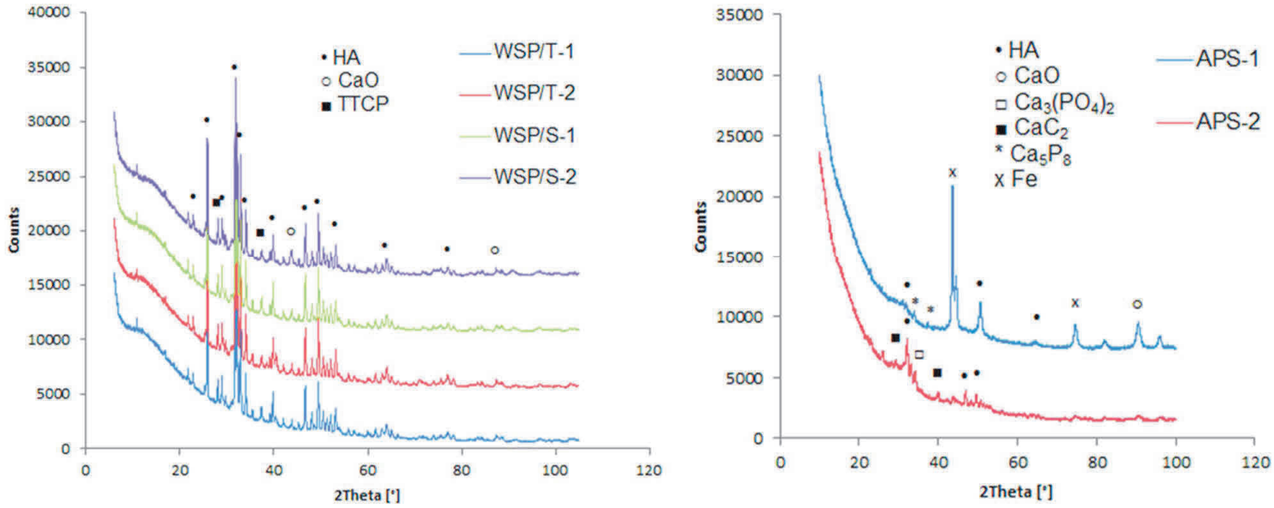

Figure 2 XRD patterns of the HA layers produced via WSP-H and APS technologies

4. CONCLUSIONS

Possibility of HA deposition by plasma spray technologies was examined in this study. Two plasma spray methods were used (hybrid water-stabilized plasma and atmospheric plasma spraying). Two different substrates for deposition by WSP-H were used.

The XRD analysis showed substantial differences in the results for each technology. While significant phase changes occurred in the coatings deposited from powder feedstock (APS), prospectively jeopardizing the potential HA use, the coatings deposited from the liquid feedstock via WPS-H technology mostly retained the original composition. Further, higher surface roughness was observed for the layer deposited by WPS-H on the steel substrate. It is assumed that deposition of WSP-H technologies may lead to more promising HA coatings with better adhesion between the substrate-coating interface and to deposition HA without cracks in layer. The results showed that WPS-H technology may be potentially suitable for deposition of biocompatible HA. Complete elimination of CaO in the deposit microstructure and increase in the coating thickness will be the aim of sequel study.

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REFERENCES

[1] KHUN, N.W., LI, Z., KHOR, K.A., CIZEK, J. Higher in-flight particle velocities enhance in vitro tribological behavior of plasma sprayed hydroxyapatite coatings. *Tribology International*. 2016, 103, 496-503. DOI: 10.1016/j.triboint.2016.08.006. ISSN 0301679x.

[2] BRINLEY, E., BABU, K., SEAL, S. The solution precursor plasma spray processing of nanomaterials. *JOM*. 2007, 59(7), 54-59. DOI: 10.1007/s11837-007-0090-8. ISSN 1047-4838.

[3] MUSALEK, R., MEDRICKY, J., TESAR, T., KOTLAN, J., LUKAC, F. *Deposition of Titania from Solution by Hybrid Water-Stabilized Plasma Torch*. In: . 2016, s. 1121-1126.

[4] FAUCHAIS, P., VARDELLE, M., GOUTIER, S., VARDELLE, A. Key Challenges and Opportunities in Suspension and Solution Plasma Spraying. *In: Plasma Chemistry and Plasma Processing*. 2015, 35(3), s. 511-525.

[5] VARDELLE, A., MOREAU, Ch., AKEDO, J., et al. The 2016 Thermal Spray Roadmap. *Journal of Thermal Spray Technology*. 2016, 25(8), 1376-1440. DOI: 10.1007/s11666-016-0473-x. ISSN 1059-9630.

[6] JORDAN, E. H., JIANG, Ch., GELL, M. The Solution Precursor Plasma Spray (SPPS) Process: A Review with Energy Considerations. *Journal of Thermal Spray Technology*. 2015, 24(7), 1153-1165. DOI: 10.1007/s11666-015-0272-9. ISSN 1059-9630.

[7] MUSALEK, R., MEDRICKY, J.,TESAR, T., KOTLAN, J., PALA, Z., LUKAC,F., CHRASKA, T., CURRY N. Suspensions Plasma Spraying of Ceramics with Hybrid Water-Stabilized Plasma Technology. *Journal of Thermal Spray Technology*. 2017, 26(1-2), 37-46. DOI: 10.1007/s11666-016-0493-6. ISSN 1059-9630.

[8] HEIMANN, R. B. Plasma-Sprayed Hydroxylapatite-Based Coatings: Chemical, Mechanical, Microstructural, and Biomedical Properties. *Journal of Thermal Spray Technology*. 2016, 25(5), 827-850. DOI: 10.1007/s11666-016-0421-9. ISSN 1059-9630.

[9] ZHOU, X., SIMAN, R., LU, L., MOHANTY P. Argon atmospheric plasma sprayed hydroxyapatite/Ti composite coating for biomedical applications. *Surface and Coatings Technology*. 2012, 207, 343-349. DOI: 10.1016/j.surfcoat.2012.07.009. ISSN 02578972.

[10] XU, J.L., JOGUET, D., CIZEK, J., KHOR, K.A., LIAO, H.L., CODDET, C., CHEN, W.N. Synthesis and characterization on atomphospheric plasma sprayed amorphous silica doped hydrxoyapatite coatings. *Surface and Coatings Technology*. 2012, 206(22), 4659-4665. DOI: 10.1016/j.surfcoat.2012.05.042. ISSN 02578972.

[11] KHOR, K.A, GU, Y.W., QUEK, C.H., CHEANG P. Plasma spraying of functionally graded hydroxyapatite/Ti-6Al-4V coatings. In: *Surface and Coatings Technology*. 2003, 168(2-3), s. 195-201. DOI: 10.1016/S0257-8972(03)00238-X. ISSN 02578972.