DEPOSITION OF TITANIA FROM SOLUTION BY HYBRID WATER-STABILIZED PLASMA TORCH

MUŠÁLEK Radek, MEDŘICKÝ Jan, TESAŘ Tomáš, KOTLAN Jiří, LUKÁČ František

Institute of Plasma Physics CAS, v.v.i. Prague, Czech Republic, EU

Abstract

Thermal spraying with liquid feedstock presents a novel route for deposition of functional coatings. In this study, possibility of preparation of titania coatings from solution by hybrid water stabilized plasma torch is presented. Coatings were prepared from solution of titanium isopropoxide $Ti[OCH(CH_3)_2]_4$ in anhydrous ethanol. Fragmentation of feedstock stream in the plasma jet was monitored by shadowgraphy. Deposition was carried out on steel samples mounted to the cooled rotating carousel. Cross-sectional images from SEM microscope showed successful formation of the deposit with dual morphology consisting of fine feather-like features combined with bigger droplets. X-ray diffraction revealed formation of nanometric rutile crystallites.

Keywords: Thermal spraying, plasma spraying, titania, solution, liquid feedstock

1. INTRODUCTION

Plasma spraying is conventionally used for spraying of powder feedstock, where powder particles are melted and accelerated towards the coated part. After the impact on the surface, coating with lamellar microstructure is produced. Another novel route is spraying of liquids where i) suspension (fine solid-state particles dispersed in solvent) or ii) solution (dissolved precursor) is sprayed. In the case of solution spraying, deposited material is, in general, produced on-site from the precursor(s), typically via emerging of the new phase from the oversaturated solution formed due to the evaporation of the solvent from the fragmented droplets. However, solution plasma spraying is a rather complex process which may incorporate numerous other phenomena such as pyrolysis, precipitation, gelation, sintering, vapour condensation, etc. [1]-[12].

For both solution and suspension spraying, substantial amount of heat is needed for proper thermal processing of the liquid in the plasma jet. Suspension/solution thermal spraying therefore benefits from spraying with torches with high enthalpy content. Hybrid water-stabilized plasma (WSP-H) technology developed at Institute of Plasma Physics CAS, v.v.i., is one of such plasma sources, which may be used for thermal spraying of liquids with considerable feed rates.

Our previous experiments demonstrated that WSP-H technology (and its predecessor WSP) may be used for effective deposition of suspensions [13], on-site reactive plasma spraying [14] or production of nanoparticles [15]. The presented study aims to experimentally demonstrate that WSP-H torch may be used also for deposition of coatings from solution. TiO_2 was selected as a material of choice due to its potential application as a functional coating, in particular for wear-resistant and photocatalytic coatings.

2. EXPERIMENTAL

Deposition was carried out with hybrid water-stabilized plasma torch WSP®-H 500 (ProjectSoft HK a.s., Czech Republic). In-house made pneumatic feeder was used to deliver liquid feedstock into the generated plasma jet. Feeding pressure, produced by compressed air, was optimized with shadowgraphy SprayCam system (Control Vision Inc, USA) which also enabled observation of the liquid stream fragmentation. Twenty AISI 304 stainless steel substrates (20 x 30 x 2.5 mm) were mounted onto rotating carousel (**Figure 1 - right**) for deposition. Half of the samples was sprayed as-received and the second half was grit-blasted with alumina grit (*Ra* ~ 6 µm). A thermocouple was attached to the back side of one of the substrates to monitor sample

temperature during preheating and spraying. In order to eliminate heat build-up, samples and carousel were cooled by a stream of compressed air.

For spraying, 1 M solution of titanium (IV) isopropoxide (Alfa Aesar, UK) in anhydrous absolute ethanol was prepared. Feeding angle was set to 25° and feeding distance to 19 mm from the torch exit nozzle. For details on injection setting, see [14]. Spraying (stand-off) distance was set to 100 mm. Solution was injected through calibrated sapphire nozzle with 0.35 mm diameter producing continuous laminar stream. Plasma torch was mounted to a robotic arm with preprogrammed trajectory. Samples were preheated to about 360 °C by 3 up&down strokes of the plasma torch without injection of the liquid. After decrease of the indicated temperature to about 280 °C, deposition was started by 3 up&down strokes followed by a brief period of cooling, after which the deposition was restarted until predefined number of deposition cycles was reached.

Cross-sections were prepared by standard materialography procedure for solution/suspension plasma sprayed coatings and then observed by SEM microscope EVO MA 15 (Carl Zeiss SMT, Germany). Phase composition of the prepared deposit was evaluated by X-ray diffraction technique of newly formed free-surfaces using D8 Discover diffractometer (Bruker, Germany) equipped with Cu anode. TOPAS software was used for Rietveld refinement method of quantitative phase analysis.

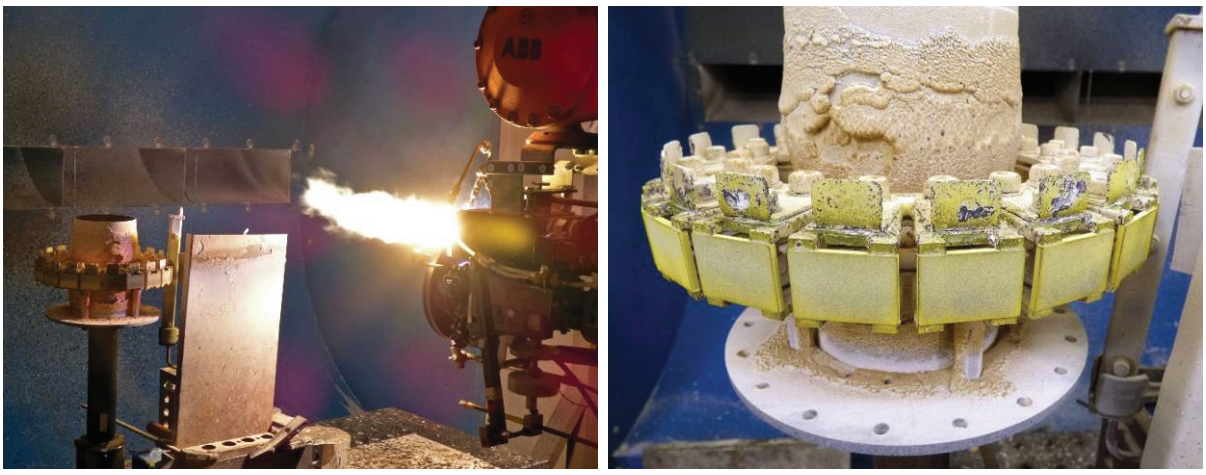

Figure 1 Deposition setup, cooling period, activated feeding (left).
Carousel with mounted samples after spraying (right).

3. RESULTS

Stream of injected solution was successfully fragmented in the plasma jet as seen by shadowgraphy (**Figure 2**), which was also used to adjust feeding pressure in order to obtain mean droplet trajectory along the axis of the plasma jet. Optimized feeding pressure was about 3.5 bars, which corresponded to approximately 100 ml / minute feed rate. After preheating, deposition cycle was repeated 5 times resulting in total in 30 deposition passes (5 x 3 x up&down robot strokes). Substrate temperature record from the deposition is illustrated in **Figure 2 - right**. At the end of each deposition cycle, substrate temperature reached 600 °C. After cooling of the substrate to about 330 °C, deposition was restarted. By this approach, overheating of the substrate could be avoided ensuring repeatability of the deposition during each deposition cycle.

Aim of the deposition was to gain adherent homogeneous coating covering whole exposed area of the samples. However, produced coatings showed limited adhesion to the substrate as they could be removed even by a soft cloth. Samples had to be therefore embedded to low-viscosity epoxy before cutting to support the deposited layer. Moreover, two different major zones of deposits were observed along the vertical axis of the mounted samples (**Figure 1 - right**) on both grit-blasted and non-blasted samples: thicker yellow coating

and thinner coating, which appeared grey. Different microstructures were observed for each zone (**Figure 3** and **Figure 4**). Grey zone showed fine microstructure with feather-like and branching features and mean thickness of about 7 µm (**Table 1**). Yellowish zone consisted of similar layer coated with additional layer of fine feather-like features intermingled with bigger micron-sized droplets with low flattening ratio. Total thickness of the yellow layer was about 20 µm.

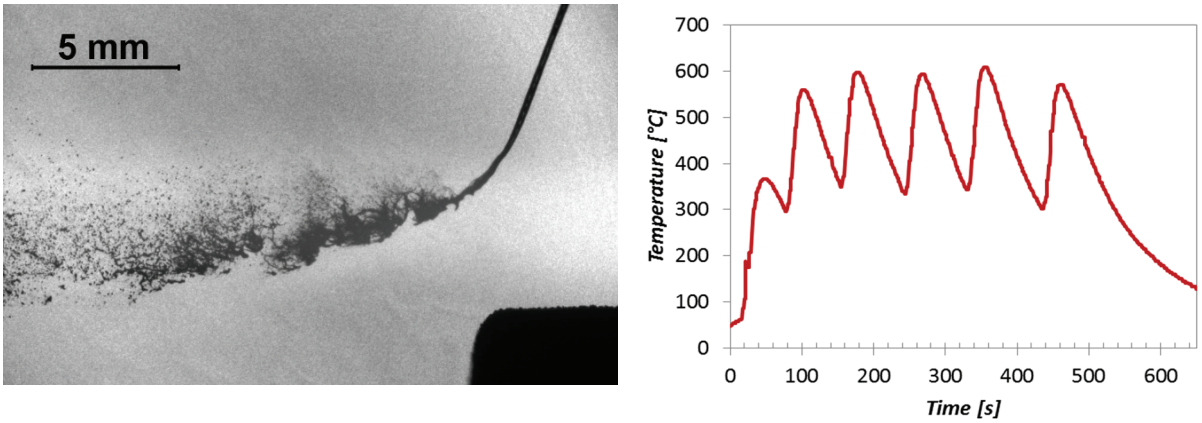

Figure 2 Solution fragmentation in the plasma jet (**left**). Note external anode of the plasma torch in the bottom-right corner and bright area of the plasma jet core. Temperature history of the sample as registered by attached thermocouple (**right**).

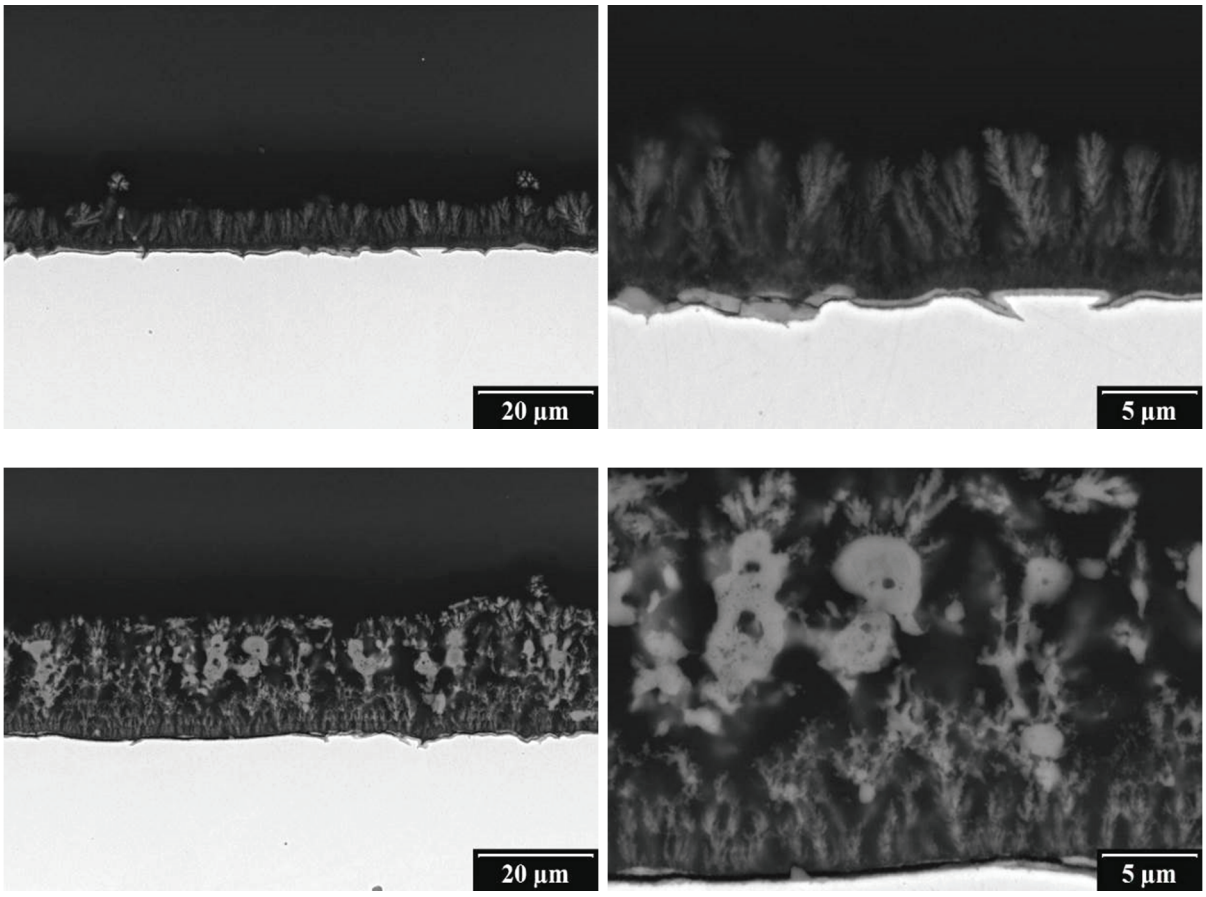

Figure 3 Microstructure of thin (above) and thick (bottom) deposit. Non-blasted substrate

For both non-blasted and grit-blasted substrates, deposits microstructure copied the substrate surface morphology, where the primary stems of the feather-like features were perpendicular to the substrate surface. Out-of-sight deposition was also observed on the sides of the samples which were not directly exposed to the plasma torch (**Figure 5**).

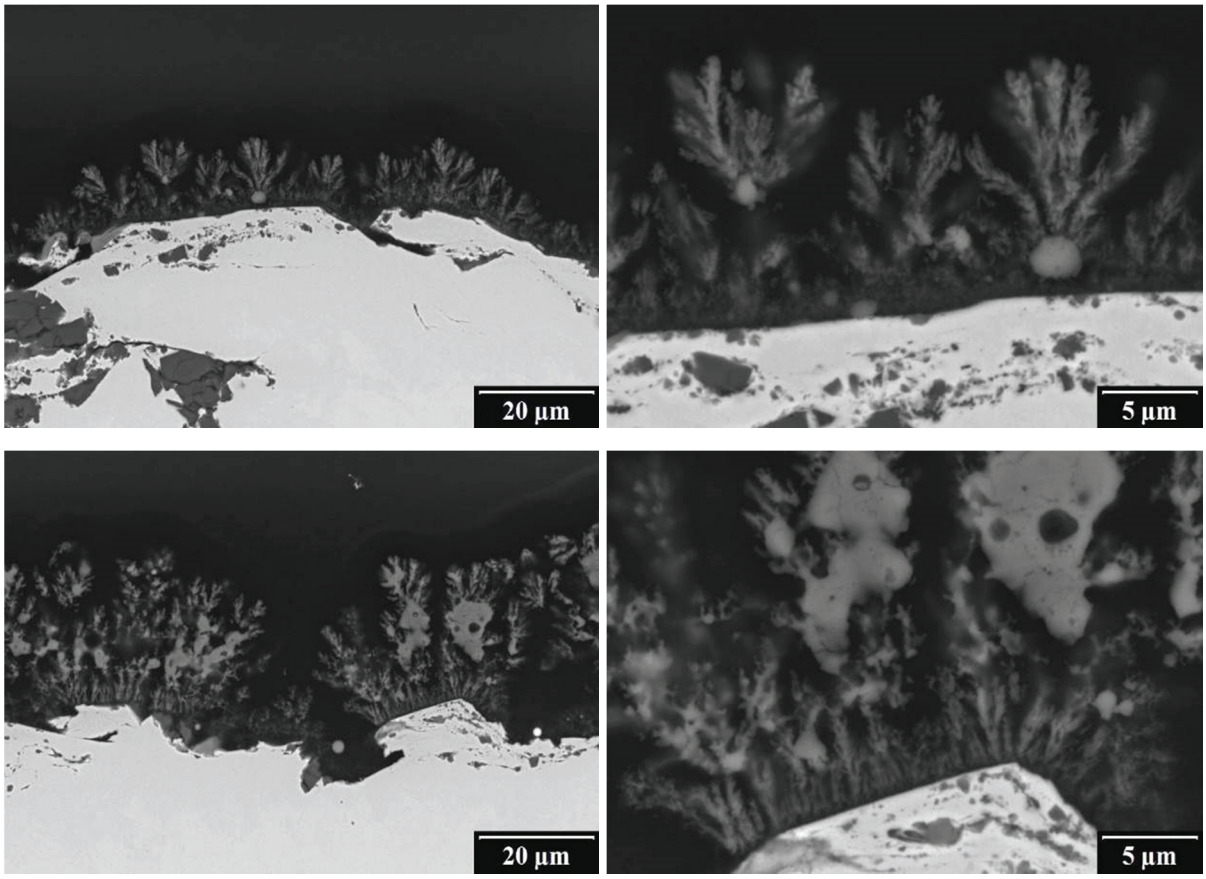

Figure 4 Microstructure of thin (above) and thick (bottom) deposit. Grit-blasted substrate

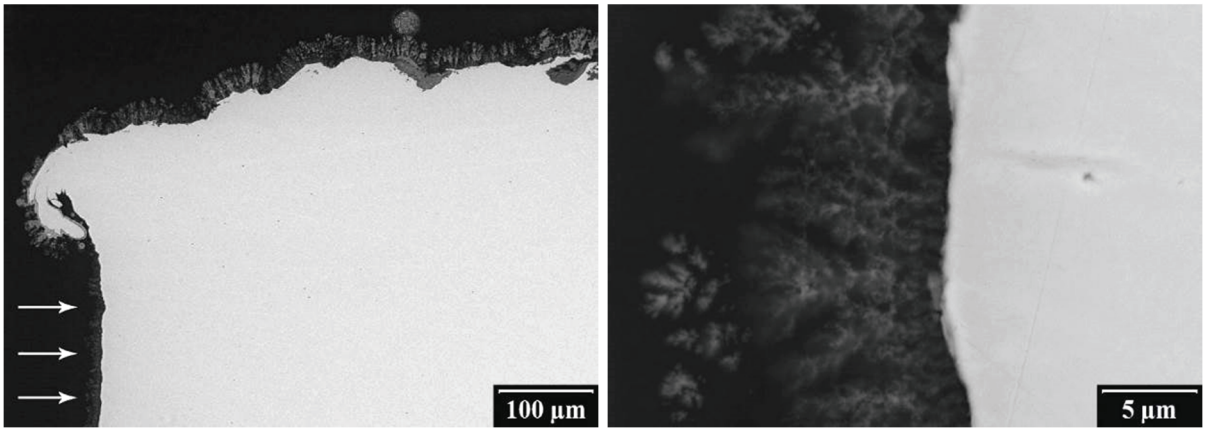

Figure 5 Out-of-sight deposition on the side (highlighted by arrows) of the grit-blasted sample

Diffraction patterns of prepared deposits (**Figure 6**) demonstrate successful formation of TiO_2. Only rutile phase was present in the deposit in considerable amount, content of anatase phase was close to the detection limit of the used method. Thanks to a relatively low thickness and high porosity of the deposit, peaks of iron

gamma were present from austenitic stainless steel substrate accompanied by corundum phase (grit-blast residues for blasted sample) or hematite residues (oxidic scale on non-blasted samples).

XRD method enabled also evaluation of the crystallite size from peak broadening by fitting of the whole diffraction patterns (**Table 1**). The crystallite size was in all cases in the range of tens of nanometers, which correlates well with SEM observation showing very fine microstructure of the deposit. The highest crystallite size was observed for thick non-blasted coating, which showed also highest content of bigger micron-sized droplets.

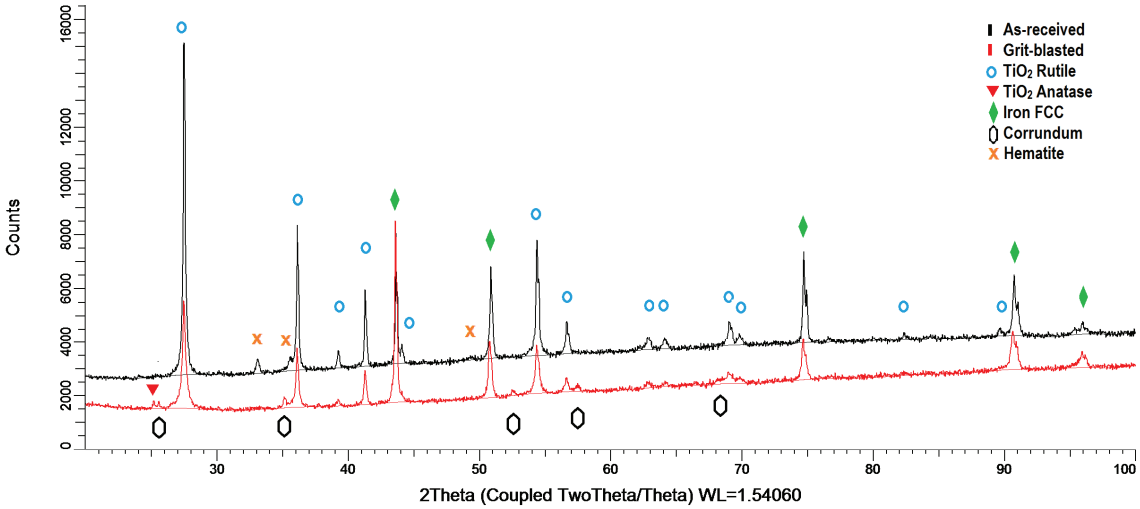

Figure 6 XRD patterns of the deposits.

Table 1 Coating thickness and crystallite size measured from XRD experiment

Deposit	Variant	Coating thickness [um]	Crystallite size [nm]
Non-blasted	thin	7 ± 1	35.1 ± 1.3
	thick	20 ± 3	66.8 ± 1.6
Grit-blasted	thin	8 ± 3	28.9 ± 0.6
	thick	23 ± 7	31.3 ± 0.5

Microstructural and XRD observations suggests that the coating was formed by two different processes: i) deposition from hot vapours condensing on the substrate and producing fine branching feather-like features, later combined with ii) deposition of larger molten droplets resulting in formation of TiO_2 splats with low flattening ratio.

Reason for the retarded occurrence of deposition of larger splats is questionable but two hypotheses may be mentioned. I) Partial clogging or displacement of the injector during deposition which disrupted the injection process. However, such major disturbance in the deposition process was not recognized during the spraying. II) Formation of TiO_2 in the feeding tank or feeding lines due to hydrolysis of solution by residual moisture present in the feedlines and compressed air.

4. CONCLUSIONS

Successful formation of TiO_2 from solution via plasma spraying with hybrid water-stabilized plasma torch was achieved. Dominant phase in the coating was rutile, only traces of anatase phase were observed. Prepared coatings possessed a very fine feather-like microstructure produced probably by combination of vapour condensation combined with deposition of bigger droplets. A high porosity of the deposit combined with lack

of contact between adjacent branches of the deposited material led to a low cohesion of the coating. Such microstructure is not suitable for applications where mechanical properties of the coating are crucial but may be promising for applications, where a large specific area of the deposit may be desirable such as catalytic functional coatings. Further optimization of the deposition process in order to obtain layers with more favorable microstructures and mechanical properties will be the aim of our next study.

ACKNOWLEDGEMENTS

This study was supported by the Grant No. GA15-12145S (Czech Science Foundation).

REFERENCES

[1] KILLINGER, A., GADOW, R., MAUER, G., GUIGNARD, A., VASSEN, R., STOVER, D. Review of new developments in suspension and solution precursor thermal spray processes. *Journal of Thermal Spray Technology*, 2011, vol. 20, no. 4, pp. 677-695.

[2] FAUCHAIS, P., VARDELLE, M., GOUTIER, S., VARDELLE, A. Key Challenges and Opportunities in Suspension and Solution Plasma Spraying. *Plasma Chemistry and Plasma Processing*, 2014, vol. 35, no. 3, pp. 511-525.

[3] CHEN, D., JORDAN, E.H., GELL, M. The solution precursor plasma spray coatings: Influence of solvent type. *Plasma Chemistry and Plasma Processing*, 2010, vol. 30, no. 1, pp. 111-119.

[4] BHATIA, T., OZTURK, A., XIE, L., JORDAN, E.H., CETEGEN, B.M., GELL, M., MA, X., PADTURE, N.P. Mechanisms of ceramic coating deposition in solution-precursor plasma spray. *Journal of Materials Research*, 2002, vol. 17, no. 9, pp. 2363-2372.

[5] CHEN, D., JORDAN, E.H., GELL, M. Effect of solution concentration on splat formation and coating microstructure using the solution precursor plasma spray process. *Surface and Coatings Technology*, 2008, vol. 202, no. 10, pp. 2132-2138.

[6] FAUCHAIS, P., RAT, V., COUDERT, J.-F., ETCHART-SALAS, R., MONTAVON, G. Operating parameters for suspension and solution plasma-spray coatings. *Surface and Coatings Technology*, 2008, vol. 202, no. 18, pp. 4309-4317.

[7] CHEN, D., JORDAN, E.H., GELL, M., MA, X. Dense alumina-zirconia coatings using the solution precursor plasma spray process. *Journal of the American Ceramic Society*, 2008, vol. 91, no. 2, pp. 359-365.

[8] XIE, L., MA, X., JORDAN, E.H., PADTURE, N.P., XIAO, D.T., GELL, M. Deposition mechanisms of thermal barrier coatings in the solution precursor plasma spray process. *Surface and Coatings Technology*, 2004, vol. 177-178, pp. 103-107.

[9] FAUCHAIS, P., MONTAVON, G., LIMA, R.S., MARPLE, B.R. Engineering a new class of thermal spray nano-based microstructures from agglomerated nanostructured particles, suspensions and solutions: An invited review. *Journal of Physics D: Applied Physics*, 2011, vol. 44, no. 9.

[10] GOVINDARAJAN, R., DUSANE, R.O., JOSHI, S. In situ particle generation and splat formation during solution precursor plasma spraying of yttria-stabilized zirconia coatings. *Journal of the American Ceramic Society*, 2011, vol. 94, no. 12, pp. 4191-4199.

[11] PAWLOWSKI, L. Suspension and solution thermal spray coatings. *Surface and Coatings Technology*, 2009, vol. 203, no. 19, pp. 2807-2829.

[12] DU, L., COYLE, T.W., CHIEN, K., PERSHIN, L., LI, T., GOLOZAR, M. Titanium Dioxide Coating Prepared by Use of a Suspension-Solution Plasma-Spray Process. *Journal of Thermal Spray Technology*, 2015, vol. 24, no. 6, pp. 915-924.

[13] MUSALEK, R., MEDRICKY, J., KOTLAN, J., TESAR, T., PALA, Z., LUKAC, F., CHRASKA, T. Plasma Spraying of Suspensions with Hybrid Water-Stabilized Plasma Technology In *ITSC 2016: International Thermal Spray Conference and Exposition*, Dusseldorf: DVS Media, 2016, pp. 267-272.

[14] KOTLAN, J., PALA, Z., MUSALEK, R., CTIBOR, P. On reactive suspension plasma spraying of calcium titanate. *Ceramics International*, 2016, vol. 42, no. 3, pp. 4607-4615.

[15] BERTOLISSI, G., BROZEK, V., CHRASKA, T., MUSALEK, R. Production of Nanoparticles Utilizing Water Stabilized Plasma Jet. In *Nanocon 2012 Conference Proceedings*, 2012, Brno: TANGER, pp. 33-38.