SUSPENSION PLASMA SPRAYING OF SUB-STOICHIOMETRIC TITANIA BY HYBRID WATER/ARGON STABILIZED PLASMA TORCH

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Abstract

In this study, suspension plasma spraying of sub-stoichiometric titania was attempted using hybrid water/argon stabilized plasma torch (WSP-H). Porous coatings with fine cauliflower-like columnar microstructure were successfully deposited in two separate experiments with different power levels of the plasma torch. In both cases, high solid-load content (40 wt. %) of the water-based suspension resulted in considerable coating thickness increase per deposition cycle. Coating annealing and partial remelting of the surface asperities were also achieved by additional pass of plasma torch in front of the coating surface. According to X-ray diffraction, all coatings consisted dominantly of rutile phase. Detailed microscopic observation of the as-sprayed and annealed deposits showed that the local coloration of the coating (ranging from dark blue to beige) was driven by the local overheating of the rough coating surface which could also promote the oxygen intake. Moreover, sample annealing was also observed to increase the sample reflectivity as observed by UV-VIS-NIR scanning spectrophotometry.

Keywords: Thermal spraying, plasma spraying, titania, suspension, liquid feedstock, WSP-H

1. INTRODUCTION

Plasma spraying with liquid feedstock (i.e. suspensions or solutions) is an alternative to conventional plasma spraying of coarse dry powders and enables deposition of novel class of layers [1]-[7]. In our previous study [8], deposition of titania combining fine coating microstructure with its large specific area was attempted from solution but the coating mechanical properties were not sufficient for engineering applications such as photocatalytic coatings. Aim of this study was to prepare a more durable titania coating, this time from suspension of slightly sub-stoichiometric titania (TiOx, $1.9 < x < 2.0$). Motivation to use this suspension was that it was a ready-to-spray suspension with commercial-grade purity and stability. Moreover, plasma spraying of common stoichiometric titania ($x = 2.0$) typically results in deficiency of oxygen content in the deposit anyway, which may be easily recognized from the coloration change (white feedstock turns into dark blue coating). If needed, such deficiency of the oxygen in the coating microstructure may be recovered by additional heat treatment in the oxygen-rich atmosphere without significant alteration of the coating microstructure.

2. EXPERIMENTAL

Hybrid water-argon plasma torch WSP®-H 500 (ProjectSoft HK a.s., Czech Republic) was used for spraying. Substrates (20 x 30 x 2.5 mm) manufactured from grit-blasted AISI 304 stainless steel were mounted for deposition to a rotating carousel cooled by compressed air. Temperature of the substrates was monitored by wireless K-type thermocouple attached to one of the substrates from the back side. Suspension of TiOx in water (Treibacher Industrie AG, Austria) with solid load of 40 wt. % was injected into the plasma jet from pneumatic liquid feeding unit through 0.35 mm diameter nozzle. The distance of the injection point from the

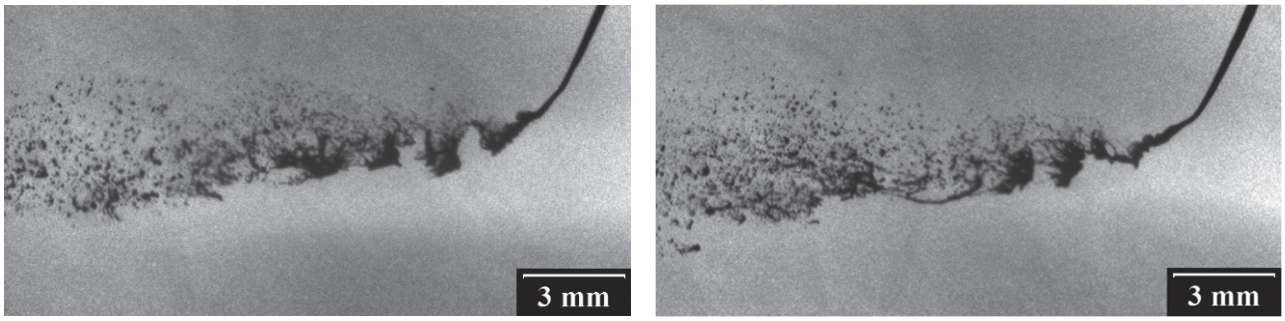
torch exit (feeding distance) was 25 mm, injection angle was 65° downstream and the torch stand-off distance was 100 mm. The feeding pressure was increased until the mean trajectory of the fragmented liquid stream, as observed by shadowgraphy system SprayCam (Control Vision Inc., USA), was identical with the plasma jet axis. After the preheating of the substrates by their exposure to the plasma jet without the suspension injection, injection was activated and deposition was carried out in 5 deposition cycles, each consisting of 3 up & down plasma torch strokes in front of the rotating sample holder. In order to evaluate sensitivity of the deposited material to the heat content provided by the plasma torch, two experiments were carried out: in the first experiment, the plasma torch was operated at standard amperage of 500 A (~150 kW torch power), in the second experiment, amperage was reduced to 400 A (~120 kW torch power).

Metallographic cross-sections and free-surfaces of the deposited samples were observed by SEM microscope EVO MA 15 (Carl Zeiss, Germany). Phase composition of the deposits was evaluated by X-ray diffraction (XRD) analysis using D8 Discover diffractometer (Bruker AXS, Germany) and quantitative Rietveld analysis.

The diffuse reflectance of the coatings was measured by a UV-VIS-NIR scanning spectrophotometer (Shimadzu, Japan) with a multi-purpose large-sample compartment. The diameter of the measured area was about 2 cm^2. The reflectance curves, obtained between 200 and 2000 nm wavelength were recorded. Prior to the measurement, a calibration process was conducted using a $BaSO_4$ reference mirror in order to minimize the error from the environment. Accuracy guaranteed by the manufacturer is ±0.3 nm for the wavelength and the uncertainty of measurement less than 0.2 %.

3. RESULTS

Successful fragmentation of the injected suspension stream in the plasma jet is apparent from **Figure 1**. For both experiments, mean particle trajectory was identical with the plasma jet axis, which is necessary for appropriate thermal treatment of the feedstock. Due to the lower plasma torch power for the 400 A experiment, optimum feeding pressure had to be reduced from 3.8 to 3.2 bars which was reflected in the slight reduction of the feed rate from 94 ml / min to 86 ml / min.



500 A 400 A

Figure 1 Shadowgraph of suspension injection into the plasma jet (bright area)

Temperature profile of the samples during the deposition as measured by thermocouple is depicted in **Figure 2**. After the preheating cycle, five deposition cycles are distinguishable as temperature peaks, each followed by the cooling period. The temperature increase during the deposition cycles was for 500 A experiment about 60 °C higher than for the 400 A experiment (i.e. 430 °C and 370 °C, respectively) which may be explained by a more intensive heat transfer from the plasma torch to the samples. Higher plasma torch power also demanded significantly longer cooling periods in order to retain the desirable interpass substrate temperature (i.e. 250 °C).

During both spraying experiments, formation of coatings homogeneously covering the substrates was achieved (**Figure 2**). Significant change of the color of the deposited material was observed during spraying from the dark blue of original suspension to the dark blue coating with beige asperities.

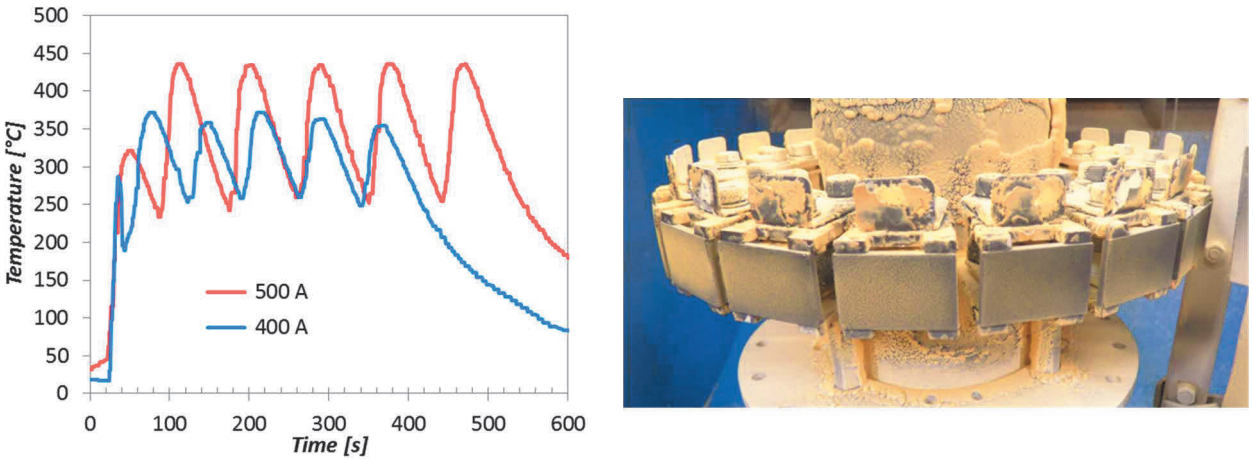
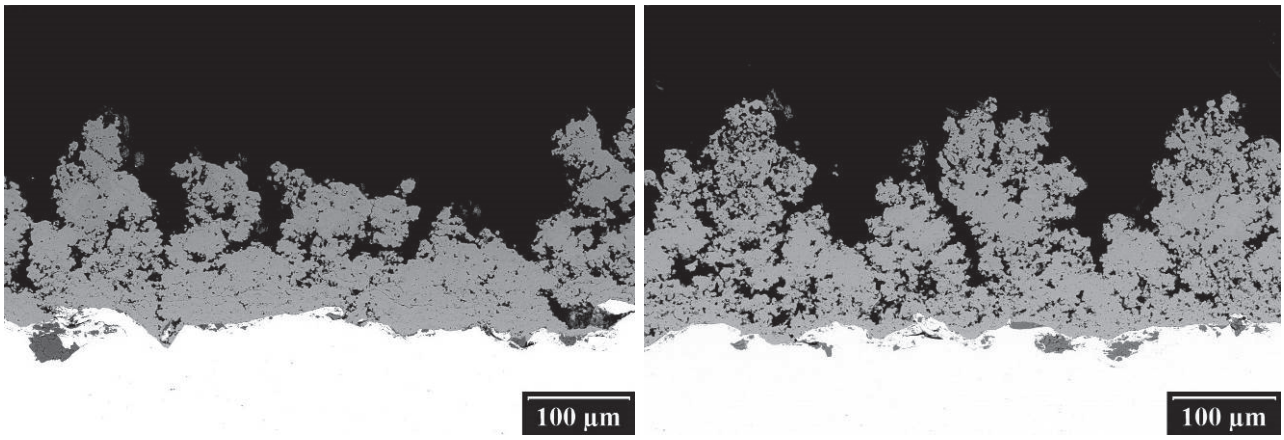


Figure 2 Left) Sample temperature history during deposition. Right) Samples after the coating deposition. Experiment 500 A

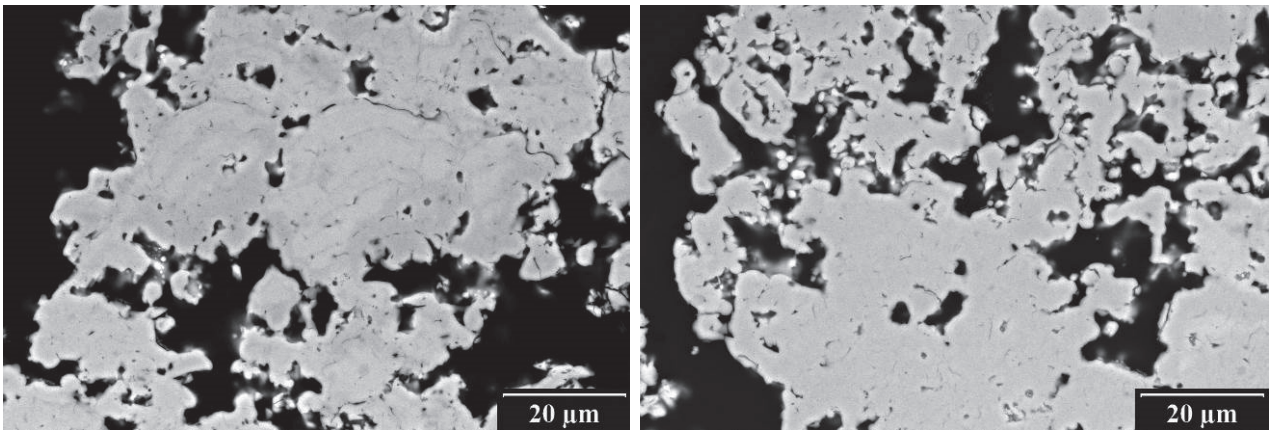
The cross-sections of the coatings revealed that both deposited coatings had similar porous cauliflower-like microstructure consisting of island of compact areas intermingled with internal porosity and delimited by deep open pores (**Figure 3**). The higher porosity of the 400 A coating leading to a looser microstructure may be explained by less heat available in the deposition process which led to less efficient formation of the splats and compaction of the deposited layer. However, islands of the well-bonded material may be observed for this coating as well (see detail in **Figure 3b**).

The final thickness of the coatings was 120 ± 44 µm and 159 ± 48 µm for the 500 A and 400 A coatings, respectively. Higher porosity of the 400 A coating may also explain its slightly higher deposition efficiency (DE) in terms of net coating thickness increase per deposition pass (about 5.3 µm/pass) when compared to the 500 A coating (about 4.0 µm/pass), however, in terms of net weight gain per pass, the DE values were comparable. Also from the free-surface side (**Figure 4**), both coatings were comparable with considerable surface roughness (**Figure 6-left**) and distinguishable splats with size ranging from submicron values to several tens of micrometers.



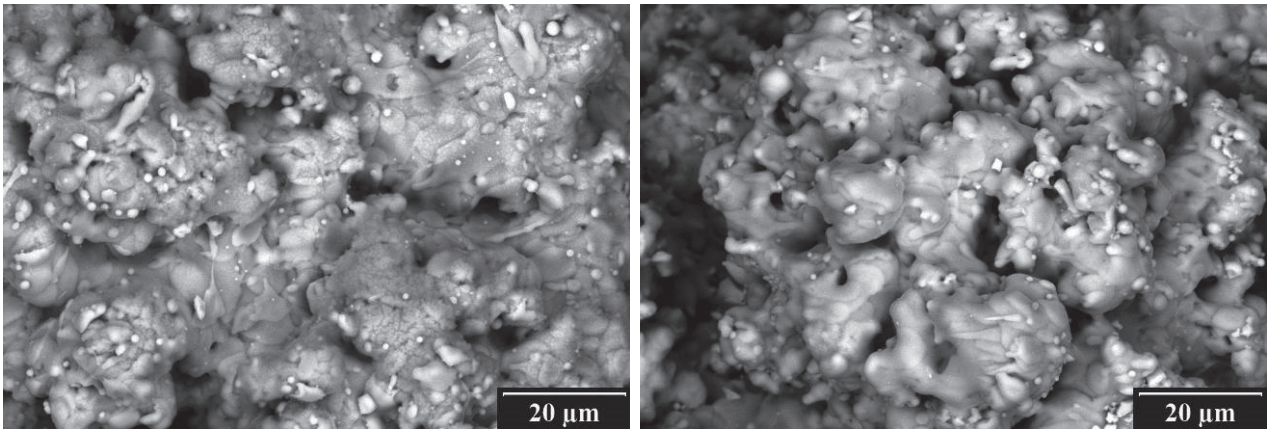
500 A 400 A

Figure 3a Cross-sections of the deposited coatings



500 A 400 A

Figure 3b Cross-sections of the deposited coatings (detail)



500 A 400 A

Figure 4 Detail of free surface of the deposited coatings

XRD analysis of both deposits showed that the coatings consisted of dominantly rutile phase (>98 wt. % according to Rietveld refinement) and only small residual amount of anatase. XRD pattern of the as-sprayed coatings indicates also presence of Magneli phase (defective rutile structure [9]).

In order to elucidate the reason for the change of coloration of the deposit, additional annealing by plasma torch was attempted. In this separate experiment, one of the 400 A samples was exposed to 3 up & down strokes of the plasma torch set again to 400 A power level but with deactivated suspension feeding. Sample temperature as measured by IR camera aiming on the carousel from the side (i.e. where the sample was due to the carousel rotation already protected from the plasma jet) showed that the sample surface temperature was at the time of full exposure to the plasma jet significantly higher than 700 °C.

Moreover, intensity of the coating beige coloration was further enhanced (**Figure 5**) and the coating surface became glossy. Comparison of the coating surface before and after annealing proves that the surface asperities were locally molten (**Figure 6)**. XRD analysis of the annealed surface showed that the anatase and Magneli phase content dropped below the detection limit of the XRD method and mean size of coherently diffracting domains (CDD) increased from about 90 nm to 200 nm, also indicating substantial modification of the coating microstructure.

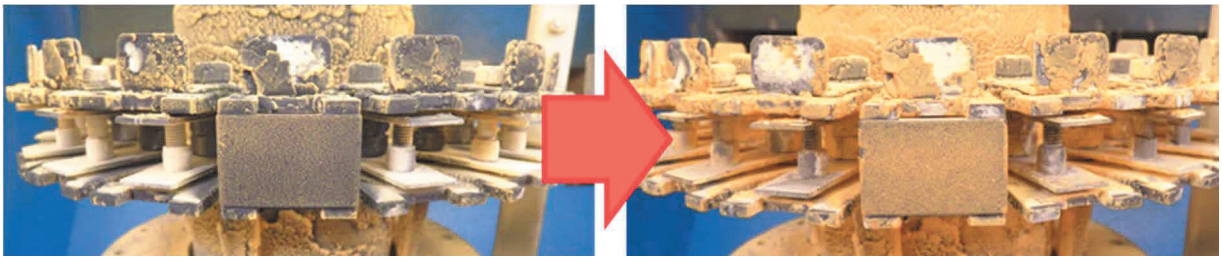


Figure 5 400 A sample before (left) and after annealing by plasma torch

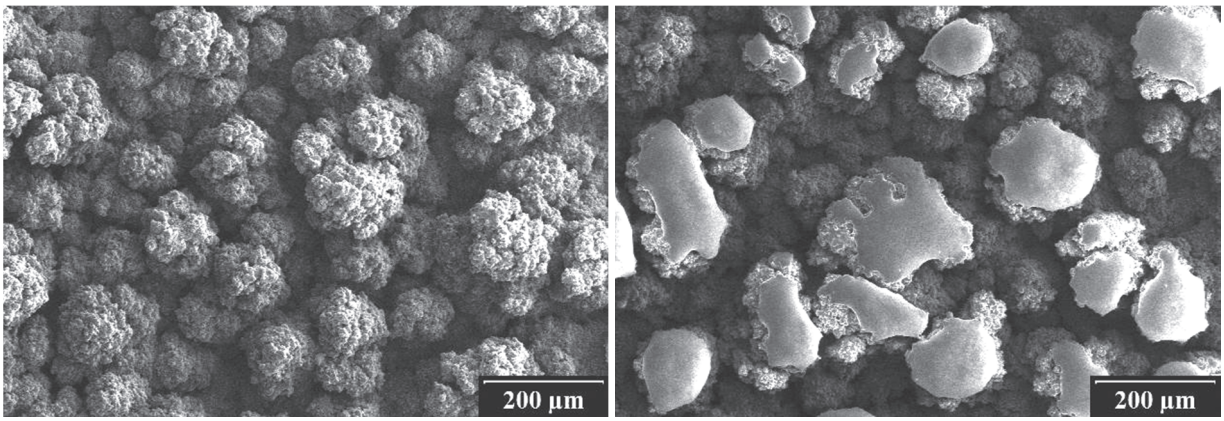


Figure 6 Free surface of the deposited 400 A coating before and after additional annealing by plasma torch

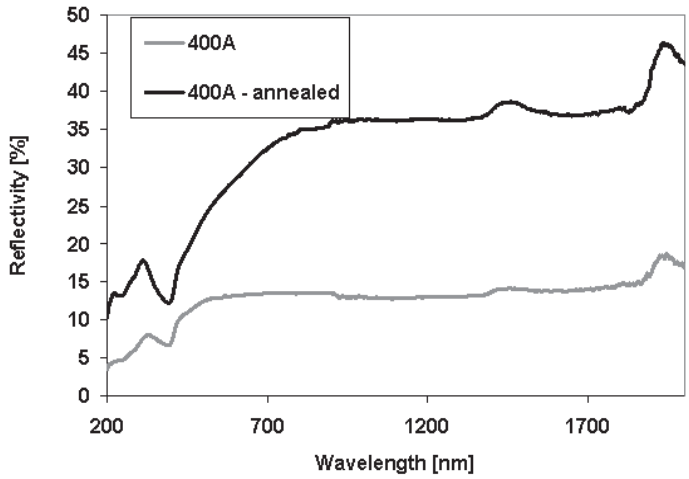


Figure 7 Reflectivity of the as-sprayed and annealed 400 A coating

Reflectivity of the coatings was measured for the as-sprayed and annealed 400 A samples. Reflectivity is expressed as the diffuse reflectance of the sample versus the diffuse reflectance of the $BaSO_4$ standard. Peaks at about 1450 nm and 1950 nm are detected due to adsorbed water. The sample annealed by the plasma torch exhibits markedly increased reflectivity that is associated with its brighter surface. Its reflectivity is higher not only in the VIS range, but also in UV and near-IR ranges, as usual when comparing as-sprayed and annealed TiO_2-based coatings [10].

4. CONCLUSIONS

This study was primarily aimed to attempt to deposit titania coatings from ready-to-spray sub-stoichiometric feedstock. This task was successfully achieved. Regardless to the plasma torch power, the dominantly rutile

layers were sprayed with considerable deposition efficiency and uniformly covered the substrate surface without any observable macroscopic failure such as delamination. Moreover, the coatings developed a rough surface with cauliflower-like microstructure which is promising for applications, where a high specific surface area of the coatings is desirable. High content of the rutile phase in the deposits is a result of thorough thermal treatment of the suspension in the plasma jet. It was demonstrated that microstructural modification of the coating may be achieved by simple additional annealing by plasma torch following immediately after the deposition. It is expected that conventional equilibrium annealing in the open air furnace could retain the coating microstructure without the local overheating of the surface asperities and also promote stoichiometry modification due to the oxygen intake. This will be also a subject of further investigation. The sample annealed by the plasma torch exhibited markedly increased reflectivity due to the deposit reoxidation and remelting of the surface asperities. Photocatalytic properties of the deposited layers are currently investigated.

ACKNOWLEDGEMENTS

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