THE ROLE OF MICROSTRUCTURE ON WETTABILITY OF PLASMA SPRAYED YTTRIA STABILIZED ZIRCONIA COATINGS

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Abstract

Atmospheric plasma spraying utilizing initial powder materials in micrometric size has been successfully used for various applications in different fields of the industry over the past several decades. Nowadays, the new trend in plasma spraying is to use sub-micron or nano-sized powder feedstocks in the form of colloidal suspension. This relatively new technology enables to obtain specific types of dense vertically cracked, fully dense or columnar microstructure. The aim of this work is to investigate the influence of coatings microstructure and topography on its water wetting properties. Two different microstructures, i.e. lamellar and columnar, were sprayed from chemically the same yttria-stabillized zirconia (YSZ) ceramics powders by the means of conventional atmospheric plasma spray and suspension hybrid water stabilized plasma spray techniques, respectively. Microstructural and phase composition of the initial powders and as-sprayed coatings were investigated using optical microscopy, scanning electron microscopy and X-ray diffraction techniques. Topography of coatings surface was measured by means of non-contact optical profilometry. The YSZ coatings wettability was evaluated based on water droplet contact angle using Sessile droplet method. The coatings microstructure reveals the important role in the change of droplet contact angle, where lamellar microstructure was found close to hydrophilic-hydrophobic transition and columnar microstructure was found superhydrophobic.

Keywords: Plasma spraying, yttria stabilized zirconia, water, Sessile drop method, contact angle

1. INTRODUCTION

Wettability of materials and coatings can be characterized by the value of contact angle or water contact angle (WCA) in the case of wetting by water. Surfaces are divided in two main categories: hydrophilic (WCA is less than 90˚) and hydrophobic (WCA is higher than 90˚) [1]. These types of coatings are widely used in daily life (e.g. antisticking and water-repellent coatings) and in industry (e.g. drag reduction and corrosion resistant coatings) [2]. Wetting behavior mostly depends on the surface chemistry and surface topography of material [3-5]. It was found out, that hierarchically (also known as dual scale) structured surface (**Figure 1**) can enhance hydrophobicity and water mobility of a surface up to superhydrophobic state (WCA is higher than 150˚) [6-8]. However, ability to be applied in the industry is a big problem of the newest hydrophobic and/or hydrophilic surface treatments and coatings production technologies because of disadvantages like: limitation in dimensions of treated details and parts due to the preparation in vacuum/inert gas chamber, impossibility of treating non-flat surfaces, etc. Plasma spraying, from this point, is a more suitable technology. Plasma spraying (atmospheric plasma spraying, suspension plasma spraying, etc.) is used in production as a way to develop different types of coatings (e.g. porous, wear resistant, corrosion resistant, thermal/environmental barrier) from metallic, ceramic, organic powders or their mixture with micron-, submicron- and nano-sized particles [9-11]. Plasma spraying of suspensions is relatively new technology which has high potential in production of hierarchically structured surfaces [2]. In this contribution, the main aim is to investigate wettability of yttria-stabillized zirconia (YSZ) plasma sprayed coatings with two different microstructures. Atmospheric plasma spraying (APS) and hybrid water-stabilized suspension plasma spraying (WSP-H) were utilized to obtain conventional lamellar (APS YSZ) and columnar (WSP-H YSZ) types of coatings microstructure, respectively.

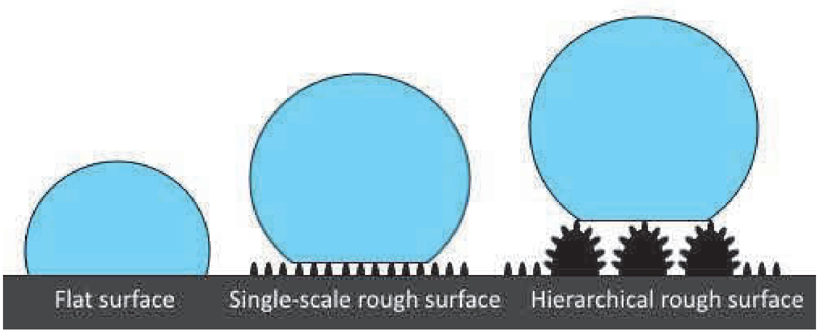

Figure 1 Wetting behavior of different surfaces: flat, single-scale rough and hierarchical rough

2. MATERIAL AND METHODS

APS MF-P-1000 (GTV) unit with a F4MB-XL plasma gun (Oerlikon Metco) spraying device was used to develop the coatings from YSZ powder (YSZ 92/8, GTV 40.23.1, GTV Gmbh). Hybrid water-stabilized plasma torch WSP-H 500 (ProjectSoft HK a.s., Czech Republic) was used to spray YSZ ethanol-based suspension with 25 wt.% of suspended solid particles. Parameters of plasma spraying process, feedstock parameters and substrate preparation for atmospheric plasma spraying were provided by powder supplier, and for hybrid water stabilized suspension plasma spraying were the same as in the work of Musalek et al. [12]. Steel coupons (diameter 25.4 mm, height 5 mm) were used as a substrate material. Substrates were grit blasted by corundum particles to activate the surface and assure the surface roughness prior to spraying with the aim of increasing the mechanical connection between the substrate and coating.

Light microscope Olympus DSX 510 together with Imaging Analysis Software and SEM Carl Zeiss EVO MA 15 were utilized to estimate plasma sprayed coatings microstructure, porosity and coatings thickness. Conventional metallography methods were used to prepare cross-sectional view of experimental specimens. Empyrean diffractometer from PANalytical was used to provide phase composition of the sprayed coatings by XRD analysis. Surface micrographs were taken by the scanning electron microscope (PHILIPS XL-30). Surface topography characteristics were obtained by MicroProf-100 optical profilometry machine (Fries Research and Technology GmbH) and Gwydion data processing (5x5 mm). Wetting behavior was defined by goniometer sessile droplet method experiment on Surface Energy Evaluation System (See System E, Advex Instruments) with image analysis software (See System for Surface Energy Measurement, Advex Instruments). Wettability evaluations were done on as-sprayed coatings. Prior to the evaluation, experimental samples were cleaned by compressed air and in ultrasonic bath. Water contact angle of dried samples was evaluated between the solid surface and constant amount of liquid (10 µl) which was deposited on the surface by micropipette.

3. RESULTS AND DISCUSSIONS

3.1. Microstructure and phase composition of the coatings

Microscopy investigation proved that deposited yttria-stabilized zirconia samples had different microstructure (**Figure 2**). Sample with columnar microstructure had almost 10 times more porosity in percentage, compared to the lamellar one (**Table 1**).

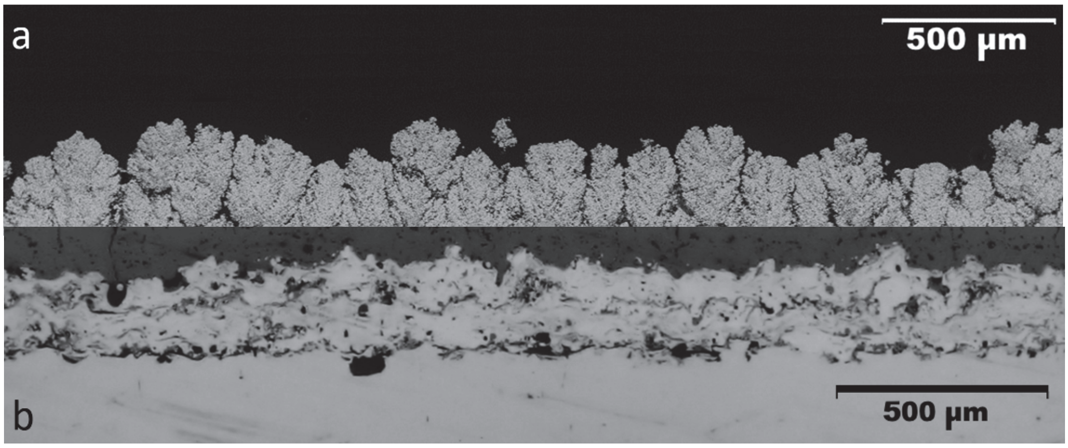

Figure 2 Cross-sectional microstructure of (a) WSP-H YSZ (SEM) and (b) APS YSZ (LM) samples

Table 1 Plasma sprayed coatings investigation result of XRD phase analysis and results of thickness and porosity evaluation

Top coat	Phases	Thickness [µm]	Porosity [%]
APS YSZ	tetragonal	235.0 ± 6.4	2.8
WSP-H YSZ	tetragonal	293.0 ± 33.0	25.0

Using liquid suspension feedstock with submicron-sized particles provided opportunity to spray columns with submicron-peaks (**Figures 2, 3**). Formation of columnar type microstructure was also observed e.g. by Sokolowski et. al. [13]. Authors studied several plasma sprayed coatings with different microstructure type and concluded, that the feedstock plays crucial role in formation of columnar microstructure: the particles size should be fine enough (e.g. submicron- or nano-sized) and suspension should have relatively low concentration of solid particles. According to the models [13, 14], small unmolten particles fly on the periphery of the plasma jet, when the coarser particles are deposited directly into the plasma jet flow. The small particles have less velocity and less kinetic energy. So at the moment of impacting the substrate surface or the previous plasma sprayed layer of the coating, particles do not splash as in the case of lamellar type of microstructure, they stick on the side of the massive columns previously formed from coarser particles. Within the spraying process, column grows with the nano- or submicron particles. In the end, these features influence the wettability of the material. Suspension WSP-H YSZ sprayed coating's surface (**Figure 3**) showed mutual structured surface as on natural superhydrophobic lotus leaf [7-8]. XRD analysis provided the information that both of as-sprayed YSZ coatings had the same phase composition (**Table 1**), what leads us to connect the topography and wettability directly in the case of plasma sprayed coatings.

3.2. Surface topography

Arithmetic roughness (R_a), root mean square roughness (S_q), Skewness (S_k), Kurtosis (K_u) and surface roughness (R_s) were measured on both deposited YSZ plasma sprayed coatings. Experimental samples topography measurements showed completely different surface parameters (**Table 2**). The surface of these two different materials structures is determined by the size of the utilized particles, distribution of peaks and valleys and their dimensions (**Figure 3**). These results may be explained by the presence of the columns of WSP-H YSZ coating. These "central" columns consist of smaller and finer columns, made from finer particles of the suspension feedstock. All of these features influenced results of surface topography investigations.

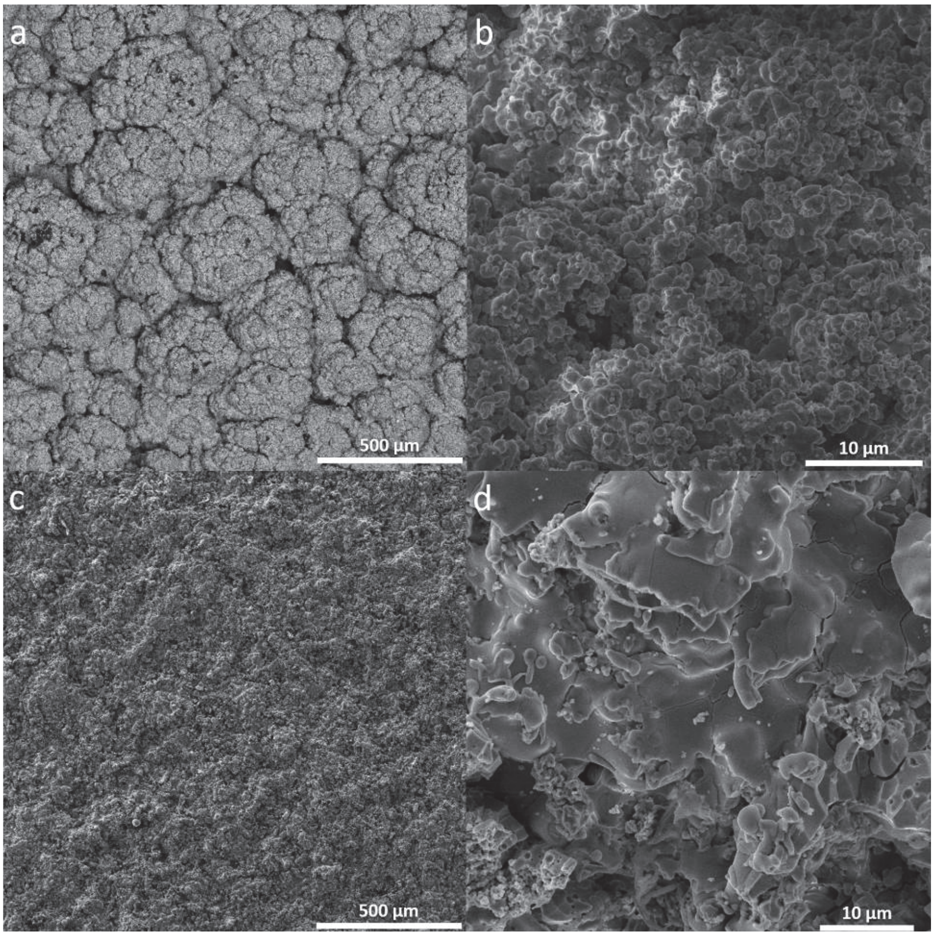

Figure 3 Top view SEM micrographs of (a) WSP-H YSZ coating, (b) detail of WSP-H YSZ coating, (c) APS YSZ coating, (d) detail of APS YSZ coating

The values of arithmetic roughness, root mean square roughness and surface roughness of WSP-H YSZ coating are much higher in comparison to APS YSZ. Surface roughness has direct influence on the wetting behavior of materials according to Wenzel and Cassie-Baxter models of wetting [4-5]. The Skewness shows that topography profile has sharp-cut peaks (if $S_k > 0$) or deep valleys (if $S_k < 0$), in the case of less obvious surface profile the Skewness is roughly equal to 0. The Kurtosis shows how narrow or wide are the valleys and peaks of the measured profile. If the Kurtosis is higher than 3, it means that surface profile has elongated (narrow) peaks or valleys, in other case ($K_u < 3$) the valleys or peaks are wider. As it was expected, Skewness showed that columnar microstructure coating had predominant number of valleys than peaks, while the surface of lamellar microstructure coating was more balanced by the quantity of peaks and valleys. Also, Kurtosis showed that the peaks on the surface of WSP-H YSZ coating are wider than of APS YSZ coating.

Table 2 Topography parameters investigations of YSZ plasma sprayed coatings with two different microstructures: R_a - arithmetic roughness; S_q - root mean square roughness; S_k - Skewness; K_u - Kurtosis; R_s - surface roughness

Coating	R_a [µm]	S_q [µm]	S_k	K_u	R_s [µm]
APS YSZ	8.8	11.1	0.005	0.141	1.289
WSP-H YSZ	45.5	54.5	-0.421	-0.598	2.372

3.3. Water contact angle measurements

WCA measurements of yttria-stabilized zirconia material, which was obtained in two different types of microstructure, showed a high dependence on the type of the coating microstructure surface topography. XRD analysis confirmed that the phase compositions of both coatings were the same, therefore the difference in water contact angle must be connected only with coatings surface topography.

Comparison of water contact angle measurement results showed that YSZ plasma sprayed coating with columnar microstructure had a high water repellence with contact angle of 156±3° (superhydrophobic) and YSZ plasma sprayed coating with lamellar microstructure was hydrophilic with contact angle of 64±3°. As it was previously mentioned, the minimum value of water contact angle for material to be called “superhydrphobic” is 150°. The water droplet behavior and its shape are presented in **Figure 4**.

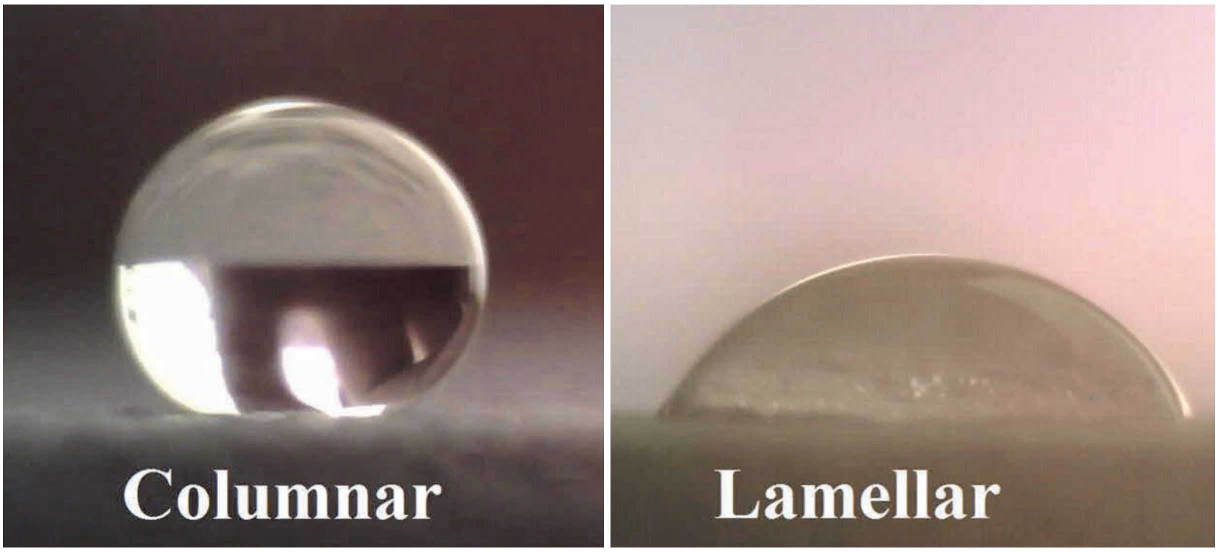

Figure 4 Water droplet behavior on the surface of columnar and lamellar types of YSZ plasma sprayed coatings microstructure

Surface topography evaluation showed that the columnar microstructure coating is more “rough” than the lamellar one. According to Wenzel and Cassie-Baxter wetting models, surface roughness has enhancing effect on the wetting behavior [4-5]. Superhydrophobicity of YSZ columnar microstructure coatings depends on the spraying parameters and feedstock features. In water stabilized suspension plasma spraying, liquid feedstock contains solid particles with the nano- and submicron size. It is clearly visible on the top view SEM micrographs (**Figure 3**) that the WSP-H YSZ coating has much finer morphology in comparison to the solid feedstock atmospheric plasma sprayed lamellar coating. The surface morphology of WSP-H YSZ coating consists of columns patterns with the layer of submicron particles on a top of the columns. Submicron particles from the feedstock form the top layer of the coating and increase the total surface area. This surface can be considered as a structured surface with hierarchical roughness (submicron- and micron-sized peaks). It was found that the top features on the surface can play critical role in wettability [2]: in between of these submicron particles (or submicron-sized peaks) there are small air pockets which do not let the liquid droplet come into the close contact with the solid surface. This explains the superhydrophobic behavior of water on columnar microstructure plasma sprayed coating.

4. CONCLUSIONS

Wettability investigation of plasma sprayed coatings with two different types of microstructure, namely conventional lamellar and columnar microstructures, showed direct influence of type of microstructure and surface topography on its wetting properties. YSZ coating with conventional lamellar structure showed hydrophilic behavior, while YSZ coating with columnar microstructure showed superhydrophobic behavior. Submicron-sized liquid feedstock contributes to the enhancement of water repellence of plasma sprayed coatings. Development of hierarchically structured surface of the coatings with superhydrophobic effect is possible by using of plasma spray technologies without any other additional surface treatments.

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