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ADVANCED HYDROPHOBIC AND HYDROPHILIC SURFACE TREATMENTS FOR NON-NUCLEAR ENERGETICS

POKROČILÉ HYDROFOBNÍ A HYDROFILNÍ POVRCHOVÉ ÚPRAVY PRO NEJADERNOU ENERGETIKU

DOCTORAL THESIS

DIZERTAČNÍ PRÁCE

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Abstract

Particular interest is given to solid surfaces with specific wetting behavior (hydrophilic/superhydrophilic and hydrophobic/superhydrophobic) due to their wide range of potential applications such as drag-reducing, anti-icing/de-icing, corrosion-resistant, anti-biofouling, self-cleaning, etc. surfaces. However, the production ways of such coatings are sophisticated multi-step procedures, which are expensive and do not provide sufficient robustness of the hydrophilic/hydrophobic wetting behavior.

The doctoral thesis is focused on (i) the development of a technological way to fabricate hydrophilic/hydrophobic coatings from wear-resistant materials utilizing thermal spraying technology; (ii) a detailed investigation of deposited coatings, analysis of their mechanical properties and the robustness of their wetting behavior.

The first part of the thesis represents a theoretical background on the wetting behavior, surface free energy, hydrophilic/superhydrophilic and hydrophobic/superhydrophobic coatings and thermal spraying technology. In the second part, Al_2O_3, Cr_2O_3-SiO_2-TiO_2, YSZ and WC-Co-Cr plasma-sprayed coatings were fabricated, and their wetting behavior was analyzed concerning their surface topography. Furtherly, several YSZ coatings with lamellar and columnar microstructures were studied to investigate the role of the microstructure on their wetting behavior. The effect of RF-plasma jet surface treatment is also presented. Finally, three different powder feedstocks of WC-Co-Cr were utilized to fabricate wear-resistant coatings with the so-called multi-scale surface topography. It was found that the combination of a coarse powder with ultra-fine (~500 nm) WC particles provides an optimal surface topography with a very high hydrophobicity that furtherly can be tuned into the superhydrophobic state after the additional Si-oil treatment. In the last part, the robustness of the wetting behavior of WC-Co-Cr samples was estimated by the slurry abrasion response test and the cavitation erosion resistance test.

Keywords

wetting behavior, surface free energy, hydrophobic coatings, superhydrophobic coatings, thermal spray technology, surface topography, wear-resistance

Abstrakt

V současnosti lze zaznamenat zvýšený zájem o studium pevných povrchů se specifickou smáčivostí (hydrofilní/superhydrofilní a hydrofobní/superhydrofobní) s ohledem na širokou škálu jejich potenciálních aplikací, mezi které patří například snížení aerodynamického odporu, ochrana proti námraze/odmrazování, korozní odolnost, ochrana proti biologickému znečištění, schopnost samočištění povrchů, apod. Způsoby přípravy takových povlaků však zahrnují sofistikované vícestupňové postupy, které jsou nákladné a neposkytují dostatečnou odolnost hydrofilního/hydrofobního chování takto modifikovaného povrchu.

Předkládaná disertační práce je zaměřena na (i) vývoj technologického způsobu výroby hydrofilních/hydrofobních povlaků z materiálů odolných proti opotřebení s využitím technologie žárového nástřiku; a (ii) studium připravených povlaků, analýza jejich mechanických vlastností a kvality smáčivosti jejich povrchu.

První část práce obsahuje úvod do teorie smáčivosti, volné povrchové energie, hydrofilních/superhydrofilních a hydrofobních/superhydrofobních povrchových úprav a přehled technologií žárových nástřiků.

V rámci druhé, experimentální, části byly připraveny povlaky na bázi Al_2O_3, Cr_2O_3-SiO_2-TiO_2, YSZ a WC-Co-Cr a analyzováno jejich smáčivé chování s ohledem na topografii jejich povrchu. Dále byly studovány povlaky YSZ s lamelární a kolumnární mikrostrukturou, s ohledem na posouzení vlivu struktury povlaku na smáčivé chování. Prezentován je zde rovněž modifikovaný povlak s využitím vysokofrekvenčního plasmatu. V závěrečné fázi experimentů byly použity tři rozdílné prášky na bázi WC-Co-Cr pro výrobu povlaků odolných proti opotřebení s tzv. více stupňovou povrchovou topografií povrchu této aktivity. V rámci bylo zjištěno, že kombinace hrubého prášku s ultra jemnými (~500 nm) WC částicemi umožňuje vznik optimální povrchové topografie s velmi vysokou hydrofobností, kterou lze dále optimalizovat do superhydrofobního stavu pomocí dodatečné modifikace olejem na bázi Si. V poslední části práce byla u tohoto typu povlaku stanovena odolnost smáčivosti vzorků WC-Co-Cr pomocí testu odezvy na otěr v abrazivní suspenzi a testu odolnosti vůči kavitační erozi.

Klíčová slova

smáčivost, povrchová volná energie, hydrofobní povlaky, superhydrofobní povlaky, technologie žárového nástřiku, povrchová topografie, odolnost proti opotřebení

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Sworn statement

I hereby declare that I have written the PhD thesis on my own following to recommendations of my supervisor Assoc. Prof. Ladislav Čelko, and it is an original work with cited literature and other professional sources listed in the text and reference list.

Pavel Komarov

Table of contents

1 Introduction

Wetting behavior, or wettability, is an essential property of the surface of solid materials. Based on the wetting behavior of water, all the surfaces can be divided into (i) superhydrophobic/hydrophobic (when water is repelled from the solid surface) and (ii) superhydrophilic/hydrophilic (when water droplets spread on the solid surface) [1]. Superhydrophobic/hydrophobic and superhydrophilic/hydrophilic surfaces are of high interest in the research field due to their wide range of potential applications where interaction with water or other liquid exists (chemical industry, machine building, machine engineering, medicine, etc.). Particular attention is focused on surfaces with robust hydrophobic and superhydrophobic behavior [2, 3].

Nevertheless, the industrial application of superhydrophobic/hydrophobic coatings is limited due to several factors: (i) such surfaces require a combination of the so-called multi-scale surface topography with low-surface energy materials; (ii) most of the superhydrophobic/hydrophobic surfaces show a lack of mechanical robustness; (iii) the majority of currently used technologies are sophisticated, expensive, time-consuming and require the use of a vacuum/inert gas chamber that constrains the treated surface in size and shape [4].

For these reasons, thermal spraying is of great potential for the fabrication of surfaces with specific wetting behavior as a relatively less sophisticated technology. Thermal spraying is already widely used in the production of wear-resistant, thermal barrier, corrosion-resistant and other types of coatings for direct application in many industrial fields.

In the present work, atmospheric plasma spraying techniques was utilized to fabricate Al_2O_3, Cr_2O_3-SiO_2-TiO_2, YSZ and WC-Co-Cr wear-resistant coatings. The wettability of the produced coatings was studied concerning their surface topography. In the next stage, YSZ coatings with a columnar microstructure were fabricated through the suspension plasma spray route using nano- and submicron-sized powders, and these were compared with conventional YSZ coatings possessing lamellar microstructure obtained by atmospheric plasma spraying. Later, the WC-Co-Cr coatings were fabricated utilizing high-velocity oxy-fuel spraying, using three different powder feedstocks: coarse powder, coarse powder with ultra-fine WC particles and fine powder with ultra-fine WC particles. The role of the surface chemical composition and surface topography on the wetting behavior of WC-Co-Cr coatings was analyzed and discussed. Finally, the robustness of their wetting behavior was studied using the slurry abrasion response test and the cavitation erosion resistance test. Additionally, several preliminary tests of superhydrophobic coatings for further potential applications were conducted and presented.

2 Review

2.1 Wetting behavior of solid surfaces

The wettability or wetting behavior of solid surfaces is commonly determined by the value of the water contact angle (WCA). Based on the WCA, all materials can be divided into four main groups: (i) superhydrophilic (WCA ≤ 10°), (ii) hydrophilic (10° < WCA < 90°), (iii) hydrophobic (90° ≤ WCA < 150°) and (iv) superhydrophobic (150° ≤ WCA) [1-3]. The most important factors that have an impact on wetting behavior are surface chemistry and surface topography.

Assessment of the wetting behavior of an ideally smooth solid surface is described by Young's equation (1) [5], where γ_{lv} is the liquid surface tension, γ_{sv} is the solid surface free energy (SFE), γ_{sl} is the solid/liquid interfacial free energy and θ_Y is the contact angle.

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} * cos\theta_Y \tag{1}$$

According to Young's theory, the hydrophobic surfaces possess high WCA and low γ_{sv} surface free energy in comparison to the hydrophilic materials.

Real objects consist of complicated micro-relief with peaks and valleys with different shapes and dimensions. Therefore, in the first half of the 20th century, Wenzel [6, 7] and Cassie-Baxter [8] proposed the equations trying to incorporate solid material rough surface in two different ways of wetting. According to Wenzel (Eq. 2), surface roughness amplifies the hydrophilicity of the intrinsically hydrophilic solid surface (when the solid surface is hydrophilic in the ideally smooth state); and amplifies hydrophobicity for intrinsically hydrophobic solid surface:

$$cos\theta_W = Rs * cos\theta_Y \tag{2}$$

where $cos\theta_W$ is the contact angle of a liquid droplet on the rough surface; $cos\theta_Y$ is the contact angle on the similar ideally smooth surface; and Rs is the surface roughness factor that shows the complexity of the surface and is expressed as the ratio "real surface area/projected surface area".

On the other hand, the Cassie-Baxter model (Eq. 3) describes the wetting behavior of the rough surface with entrapped air pockets existing in between the liquid and solid phase, where the liquid contact with a solid surface exists only at a small surface area and can be represented by the equation (3):

$$cos\theta_{CB} = f_s * cos\theta_Y + f_s - 1 \tag{3}$$

where $cos\theta_{CB}$ is the contact angle between a liquid droplet and a rough surface; and f_s is the part of the surface area that is in contact with a liquid droplet.

The combination of Wenzel and Cassie-Baxter models (Eq. 4) was found to be helpful in the description of the wetting behavior of solid surfaces with the multi-scale roughness [9], where the surface roughness factor Rs and the surface area of "solid-liquid" contact f_s are considered:

$$cos\theta_{CBW} = Rs * f_s * cos\theta_Y + f_s - 1 \quad (4)$$

2.2 Development of surfaces with specific wetting behavior

Most well-known and widely used construction materials, such as metals and ceramics, are hydrophilic due to their high surface free energy (metals) and polar components (ceramics). In the review [10], it is reported that only several solid material surfaces possess almost superhydrophilic behavior (WCA ~ 10° or below): gold, copper, chromium, TiO_2, quartz, amorphous silica and glass. For other less hydrophilic or even hydrophobic materials, two common approaches of hydrophilization are used: (i) deposition of more hydrophilic molecular structures than the base material (in the case of inorganic base materials); or (ii) modification of the surface chemistry i.e., increasing of SFE (in the case of polymers with low SFE) [10].

The manufacture of the hydrophobic/superhydrophobic surfaces is inspired by various natural surfaces, and based mainly on the surface treatment to deposit low surface energy materials and/or to form multi-scale surface topography [11, 12]. Plenty of methods were applied to develop superhydrophobic surfaces including lithography, solution immersion, plasma etching, templating, electrodeposition, sol-gel, etc. [12, 13]. Significant attention was recently focused on the rare-earth elements' oxides (REO's) due to the work reported by Azimi et al. [14], where REO's were presented as ceramics with intrinsically hydrophobic behavior in the polished state due to their unique electronic structure. Further research on this topic shows significantly varying results which keep the hydrophobicity of REOs under debate [15-18].

2.3 Application of surfaces with specific wetting behavior

Particular attention is focused on surfaces with robust hydrophobic and superhydrophobic behavior. Such surfaces are highly attractive due to the possibility to provide (i) water-oil separation (as a mesh or filters where a superhydrophobic-oleophilic surface interacts with oil, but repels water); (ii) self-cleaning (dust and ultra-fine particles are collected during the sliding of water droplets giving higher performance of solar cells); (iii) anti-icing/de-icing (to prevent ice accumulation or decrease ice adhesion in off-shore components, parts of an aircraft, and wind mills where ice affects their productivity and/or might be a cause of a crash of an aircraft); (iv) self-condensed microdroplets (hydrophobic surfaces are intended to provide drop-wise condensation mechanism of heat transfer that is almost 10 times more effective than film-wise mechanism that typically occurs on currently used hydrophilic metallic surfaces); (v) anti-biofouling (hydrophobic/superhydrophobic surfaces have a smaller contact area with water in comparison to hydrophilic surfaces, giving less space for micro-organisms to attach and grow on the surfaces of the parts of the ships that are in long-term contact with water); (vi) increased corrosion resistance (as superhydrophobic/hydrophobic surfaces have a smaller contact area with liquid); (vii) drag-reduction (low adhesion of water to the hydrophobic/superhydrophobic surfaces decrease an energy loss during movement of the ships and submarines), etc. [2, 3].

However, most of the methods used to manufacture the coatings with specific wetting behavior have several major disadvantages that limit their industrial-scale application, such as the time-consuming nature of the process or constraints on the size and shape of treated components, due to the required vacuum or inert atmosphere chamber, the insufficient mechanical stability (e.g., low wear resistance of fluoropolymers) [19], degradation in the harsh atmosphere, or even in the sunlight, and high technology costs associated with the purchasing cost of rare-earth element oxides and their precursors [12, 20, 21].

Therefore, developing cost-effective and industrially scalable technology for the fabrication of mechanically durable surfaces with a robust specific wetting behavior remains challenging.

2.4 Thermal spray technology

Thermal spraying is a potential candidate for the manufacturing of coatings with specific wetting behavior. It is a highly industrialized, relatively fast and cost-effective way to deposit coatings on a large scale. This technology is widely used in the fabrication of porous/dense, wear-resistant/abradable, corrosion-resistant, thermal/environmental barrier, and other types of coatings from metallic, ceramic, cermet, and polymer materials. During thermal spraying, a feedstock material (wire, powder or suspension) is fed to a plasma or a flame jet followed by heating and acceleration of particles towards the substrate. Thus, the formation of the coating is a result of the plastic deformation of accelerated melted, partially melted, or un-melted particles that impacted the substrate surface. Using thermal spraying enables the deposition of coatings with a thickness ranging from several micrometers up to a few millimeters.

The group of thermal spraying methods consists of several technologies the most important ones are atmospheric plasma spraying (APS), water-stabilized plasma spraying (WSP-H), high-velocity oxy-fuel spraying (HVOF), high-velocity air-fuel spraying (HVAF), flame spraying (FS), twin wire arc spraying (TW), detonation-gun spraying (D-Gun) and cold-gas dynamic spraying (CG or CGS). There also exist certain modifications of these technologies based on the type of the feedstock (e.g., powders suspension and/or precursors solution) and the surrounding atmosphere (vacuum/low pressure): suspension plasma spraying (SPS), solution precursor plasma spraying (SPPS), vacuum plasma spraying (VPS), low-pressure plasma spraying (LPPS), suspension high-velocity oxy-fuel spraying (S-HVOF), etc.

3 Aims of the thesis

The main aim of the thesis is to develop a technology to fabricate wear-resistant hydrophobic/hydrophilic coatings employing the thermal spraying process; and to provide the detailed analysis of the produced coatings, assessment of their mechanical properties and robustness of the wetting behavior.

To fulfill the main aim of the thesis, the following steps were designed and performed:

- Spraying of wear-resistant coatings from commercially available powders, namely Al_2O_3, Cr_2O_3-SiO_2-TiO_2, ZrO_2-Y_2O_3 (YSZ) and WC-Co-Cr using APS technique;
- Study of the plasma sprayed coatings in the as-sprayed state and after #220 abrasive paper, 9 µm, 3 µm and 1 µm diamond suspensions (grinding and polishing) in order to determine a correlation between surface topography parameters and water wetting behavior;
- Spraying of YSZ coatings using ultra-fine powder particles in suspension feedstock to study the effect of different types of microstructure (lamellar vs. columnar) onto wetting behavior in the as-sprayed state;
- Improvement of the wetting behavior up to superhydrophobic state of suspension plasma sprayed YSZ coatings via additional surface modification;
- Investigation of the fabricated modified and unmodified YSZ coatings via SEM, EDX, topography analysis, and determination of their water contact angles;
- Fabrication of the wear-resistant WC-Co-Cr coatings from three different powders (coarse, coarse with ultra-fine WC, and fine with ultra-fine WC) employing HVOF spraying in order to obtain multi-scale surface roughness;
- Development of a technologically simple way to amplify hydrophobicity of the coatings surface;
- Detailed characterization of the WC-Co-Cr coatings through SEM, EDX, XRD, XPS and assessment of topographical features, water contact angles and surface free energies in four states, namely (i) as-sprayed, (ii) as-sprayed modified, (iii) polished and (iv) polished modified;
- Carrying out the slurry abrasion response test and cavitation erosion test on the WC-Co-Cr coatings in the as-sprayed and as-sprayed modified states to estimate the robustness of the wetting behavior.

4 Experimental design and methods

In order to fulfill the aims and obtain the results, structural observation, surface chemistry and phase analysis, surface topography investigation, water contact angle measurements, free surface energy evaluation, wear-resistance and cavitation erosion tests were conducted. The flowchart of the experimental design is presented in Figure 1.

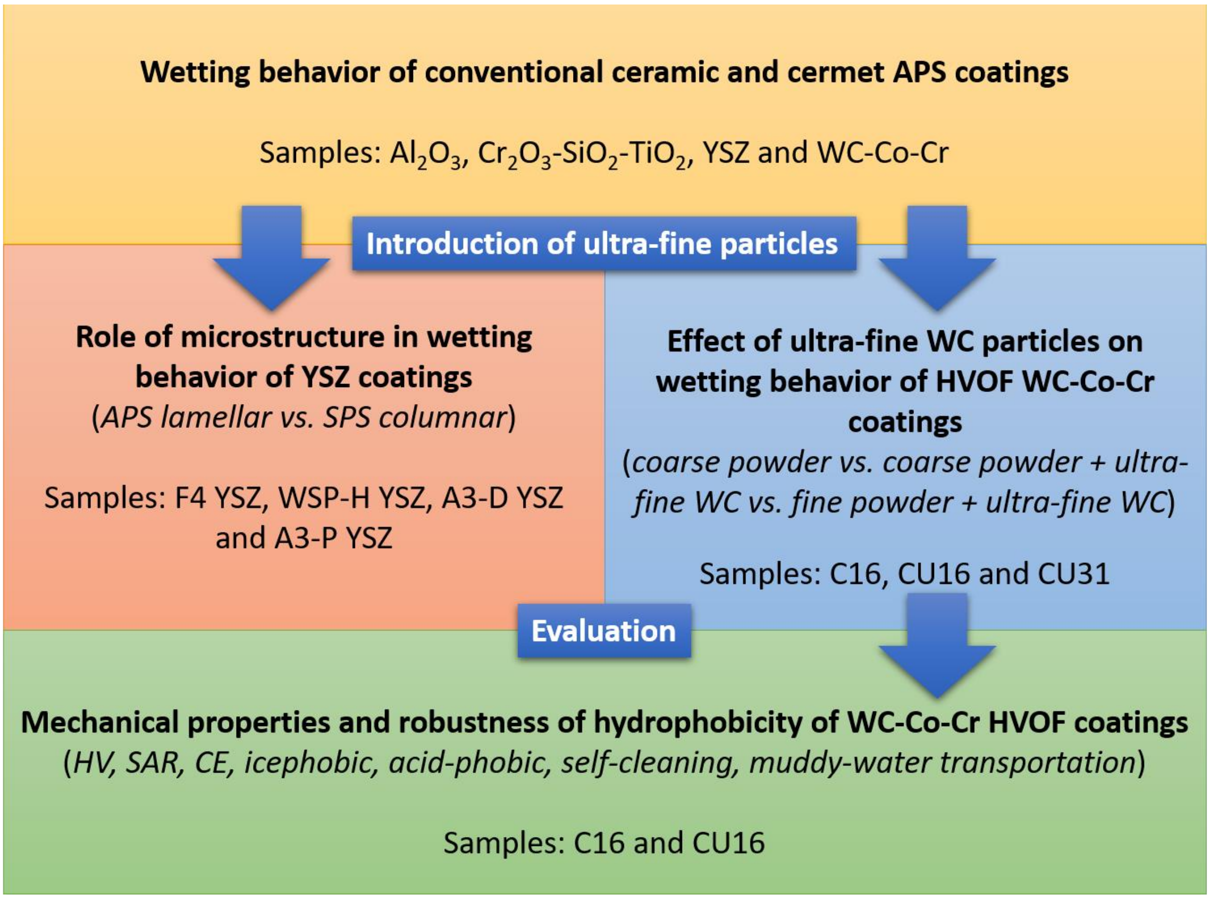

Figure 1 The flowchart of the experimental design used in the present work

At first, it was decided to make screening and spray commercially available wear-resistant ceramic (Al_2O_3, Cr_2O_3-SiO_2-TiO_2, ZrO_2-Y_2O_3 (YSZ)) and cermet (WC-Co-Cr) powders by using the APS technique. This step was done with the aim of obtaining the first experience on how the water will behave on a surface of conventional coatings widely used in the industry. The spraying process of all aforementioned powders was performed in cooperation with S.A.M. – metalizační společnost s.r.o. (Brno, Czech Republic).

Based on the obtained results, YSZ and WC-Co-Cr materials were selected for further research: (i) to estimate the influence of different parameters of plasma spraying of YSZ powder and suspension with ultra-fine particles on coating microstructure and wetting behavior; (ii) to investigate the wettability of WC-Co-Cr coatings fabricated by HVOF spraying utilizing three different feedstocks (coarse powder, coarse powder with ultra-fine WC and fine powder with ultra-fine WC); and (iii) to provide additional surface treatment. In this research stage, spraying of YSZ suspension was done at the Institute of Plasma Physics of the Czech Academy of Science (Prague, Czech Republic) and at the Institute of Energy and Climate Research, Forschungszentrum Jülich GmbH (Jülich, Germany).

The final part of the experimental work focused on evaluating the mechanical performance of the produced WC-Co-Cr coatings and assessing the robustness of their wetting behavior, including short-term testing on icephobic, acid-phobic, muddy-water transportation and self-cleaning performance.

5 Results and Discussion

5.1 Wetting behavior of YSZ, Al_2O_3, Cr_2O_3-SiO_2-TiO_2 and WC-Co-Cr plasma sprayed coatings

Analysis of cross-sections of atmospheric plasma sprayed coatings showed that the coatings consisted of compact splat-like or lamellar microstructure with a low number of unmelted particles, see Figure 2. Based on the results of the digital image analysis, the thickness of the coatings was in a range from ~290 μm to ~780 μm and the porosity ranged from ~3 % to ~7 %.

Analysis of wetting behavior was performed on ceramic and cermet coatings in the as-sprayed state, after grinding with #220 abrasive paper and after polishing with diamond suspensions containing 9, 3 and 1 μm abrasive particles.

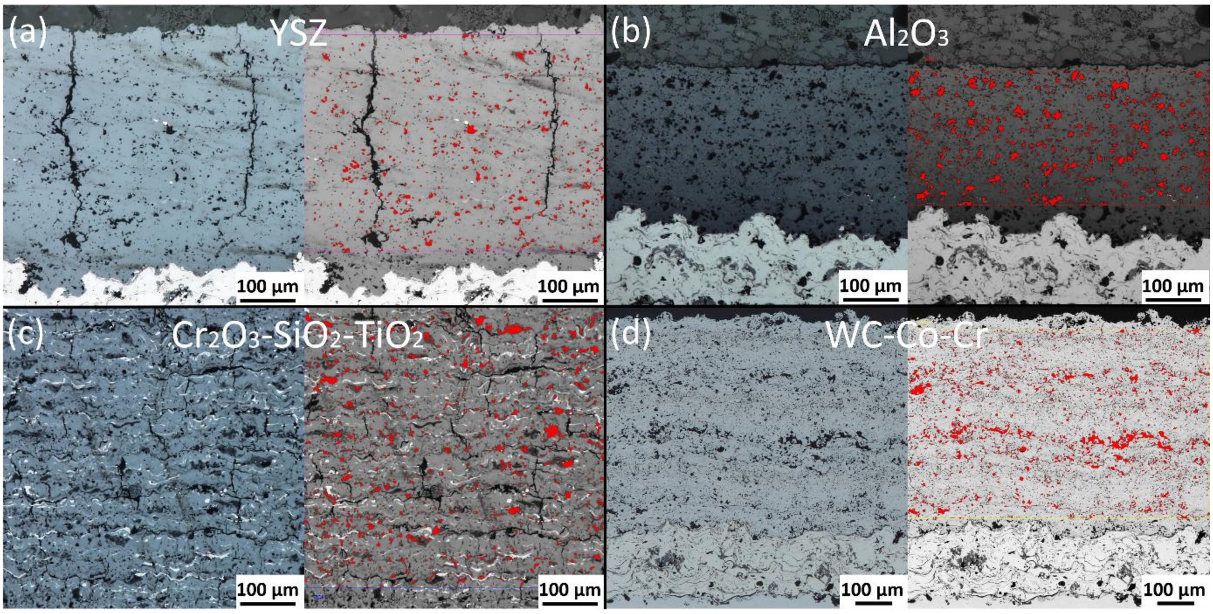

Figure 2 Cross-sections of (a) YSZ, (b) Al_2O_3, (c) Cr_2O_3-SiO_2-TiO_2 and (d) WC-Co-Cr coatings; pores are marked by red color

All YSZ, Al_2O_3, Cr_2O_3-SiO_2-TiO_2 and WC-Co-Cr plasma sprayed coatings revealed hydrophilic behavior in the as-sprayed, ground and polished surface states with a water contact angle (WCA) below 90°. The wetting behavior of ceramic coatings in the as-sprayed and polished states was found to be similar. The most significant difference in WCA between different surface states, as well as the highest WCA value, was observed for the cermet WC-Co-Cr coating, namely from ~89° in the as-sprayed state down to ~55° after grinding and up to ~73° in the polished state.

It was observed that the WCA values continued decreasing over time. All the coatings showed similar WCA values ranging from ~50° up to ~79° after 300 s of measurements in the as-sprayed, ground and polished states. The effect of water absorption on plasma sprayed oxide ceramic coatings in the polished state was observed by Harju et al. [22]. The smallest change in the WCA value with the time was noticed on the YSZ ceramic coating. Though, the porosity of the YSZ coating was the lowest among all the studied coatings, the decrease of the WCA value over the time was connected to the presence of vertical cracks, see Figure 2a.

The effect of coatings porosity/cracks on wetting behavior among all the coatings was dominant compared to the surface topography state. Therefore, no clear evidence of the surface topography influence on wetting behavior was observed at the end.

The studied coatings were mostly ceramics that are polar components and supposed to be hydrophilic due to the strong polar-polar interactions [10]. However, the highest value of WCA (more hydrophobic), as well as the highest surface roughness factor *Rs*, was observed for the as-sprayed surfaces. It shows that wetting did not follow the Wenzel model, but followed the Cassie-Baxter model (Eq. 3) at the moment of first contact of the water droplet with the solid surface. Consequently, it can be suggested that the WCA value of intrinsically hydrophilic materials might be increased (toward hydrophobicity) if the Cassie-Baxter wetting state is reached and the penetration of water into the pores/valleys/cracks is prevented. Achievement of the long-term stable Cassie-Baxter wetting state is possible when the surface roughness has the multi-scale character, with nano- and submicron-sized peaks/valleys [9].

Based on the results obtained from this study, further research is focused on the formation of YSZ and WC-Co-Cr coatings with a multi-scale topography, with the aim of trying to amplify coatings hydrophobicity. In order to ensure the formation of the multi-scale surface roughness, it was decided to introduce ultra-fine powder particles into the initial feedstock. To realize that, (i) YSZ coatings were produced by the means of suspension plasma spraying (SPS), utilizing ultra-fine powder particles; and (ii) bi-modal (combination of the coarse and ultra-fine powder particles) feedstock was used in the case of WC-Co-Cr material to fabricate the coatings by the use of high-velocity oxy-fuel (HVOF) spraying.

5.2 Investigation of wettability of YSZ plasma sprayed coatings with different microstructure

Yttria-stabilized zirconia (YSZ) material was used in the form of solid and liquid feedstocks to manufacture coatings with different microstructures, namely lamellar and columnar, and to investigate the effect of surface topography and microstructure on wetting behavior. The conventional route of spraying of YSZ powder was used to fabricate the coating with a lamellar microstructure (sample F4 YSZ), using atmospheric plasma spraying utilizing the F4 plasma torch. An in-house-made ethanol-based suspension with YSZ ultra-fine powder particles was used to develop YSZ coatings with the columnar microstructure (samples WSP-H YSZ, A3-D YSZ and A3-P YSZ), employing the water-stabilized WSP-H and Axial III plasma torches.

The F4 YSZ sample consisted of a conventional lamellar microstructure with a low number of unmelted particles and a relatively low porosity (~3%). The WSP-H YSZ sample consisted of a columnar or cauliflower-like microstructure, with clearly distinguishable columns separated by inter-columnar voids. Cross-sectional observation of Axial III suspension plasma sprayed YSZ coatings revealed that the A3-P YSZ sample consisted of a columnar microstructure with clearly separated columns. In contrast, the A3-D YSZ sample was of a denser columnar microstructure, with a lower number of gaps/pores between columns. However, the presence of inter-columnar voids at the surface of A3-D/A3-P YSZ samples was not observed when compared to the sample WSP-H YSZ. The surface topography of the WSP-H, A3-D and A3-P YSZ samples consisted of a multi-scale topography with massive coarse columns (~30-200 µm in size) covered by submicron-sized particles.

The analysis of XRD patterns revealed that all the YSZ coatings consisted of the metastable tetragonal phase (t` - YSZ). The EDX analysis showed the presence of zirconium, oxygen and yttrium elements, and the distribution of elements was found to be very similar for all the YSZ coatings: 59-61 wt.% of zirconium, 14-15 wt.% of yttrium and 24-26 wt.% of oxygen. The results of the XPS analysis showed no significant difference among the samples, and revealed the highest content of Zr 3d (69-70 at.%), then O 1s (~17 at.%) and Y 3d (4-5 at.%), which is the base of YSZ (ZrO_2-Y_2O_3). The C 1s element was detected due to the organic contaminations adsorbed from the atmosphere and/or the vacuum chamber of XPS apparatus [23].

The lamellar F4 YSZ sample was found to be hydrophilic with a WCA of 64 ± 3° and the columnar WSP-H YSZ sample was superhydrophobic with a WCA of 156 ± 3°. The YSZ coatings with columnar microstructure fabricated employing an Axial III plasma torch showed hydrophobic behavior in the A3-D YSZ sample (with WCA of 129 ± 3°) and almost superhydrophilic behavior in the A3-P YSZ sample (with WCA of 14 ± 7°). As the XRD analysis of the YSZ coatings showed the same phase composition with only a single tetragonal-YSZ phase, the elemental distribution (the EDX and the XPS analyzes) was found to be very similar, therefore, such a high difference in wetting behavior was mostly related to the difference in microstructure and topography. The results of surface topography measurements are summarized in Table 1.

Table 1 Roughness parameters of surfaces of YSZ coatings

Coating	Sa [μm]	Sq [μm]	Ssk [-]	Sku [-]	Rs [-]
F4 YSZ	7.3	9.1	0.14	2.81	1.29
WSP-H YSZ	41.8	52.4	-0.93	3.45	3.56
A3-D YSZ	28.3	34.0	-0.05	2.31	2.56
A3-P YSZ	30.1	35.9	-0.21	2.35	2.65

The surface of the lamellar F4 YSZ sample was composed of the splats of several tens of microns in size and pores/cracks in between of them. This combination provided hydrophilic wetting behavior following the Wenzel wetting model (Eq. 2), with pores/cracks filled by water, resulting in the low WCA value (hydrophilicity). According to the Wenzel model, the surface roughness factor *Rs* can amplify hydrophobicity/hydrophilicity. It explains the reason for the lower WCA value of the A3-P YSZ sample compared to the WCA value of the F4 YSZ sample (WCA = 14 ± 7° and *Rs* = 2.65 vs. WCA = 64 ± 3° and *Rs* = 1.29, respectively).

Figure 3 represents the height-maps of the A3-D, A3-P and WSP-H YSZ samples with the averaged arithmetical mean height *Ra* roughness parameter measured on 5 random places on the top of the columns. The microstructures of the WSP-H YSZ and A3-P YSZ coatings are relatively similar, but the WCA values are significantly different (156 ± 3° vs. 14 ± 7°). The difference in the wetting behavior was connected to the fact that the surface of the large columns of the WSP-H sample (*Ra* = 1.6 μm) was much rougher compared to the A3-P/A3-D YSZ samples (*Ra* = 0.6 μm).

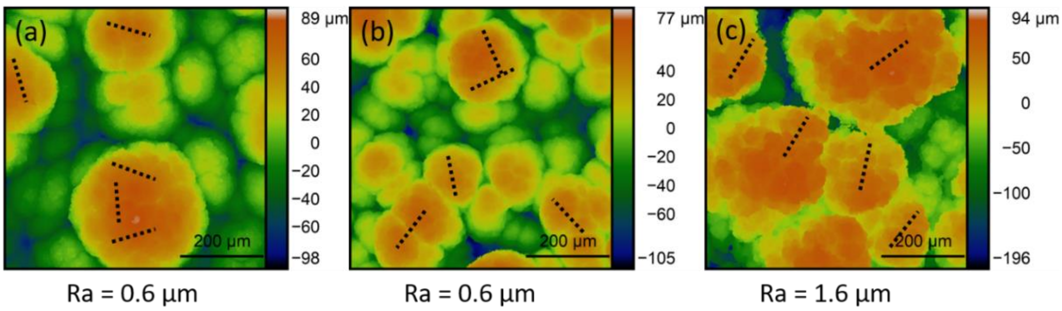

Figure 3 Height-maps of (a) A3-D, (b) A3-P and (c) WSP-H YSZ samples; the dashed lines (~100 μm) mark the profiles used for *Ra* measurements

It can be concluded that (i) the lamellar microstructure of the YSZ (F4 YSZ sample) coatings provided hydrophilic behavior with the Wenzel wetting state due to the infiltration of water into pores and cracks in the coating; (ii) the presence of pores between flat columns supported almost superhydrophilic behavior with the Wenzel wetting state in the A3-P YSZ sample; (iii) similar flat columns, but with a denser columnar microstructure in the A3-D YSZ sample prevented the penetration of water into the coating, resulting in hydrophobic behavior with a Cassie-Baxter wetting state; and (iv) the rough surface of the columns as well as the high surface area of the WSP-H YSZ sample provided superhydrophobic behavior with a Cassie-Baxter wetting state.

As wetting behavior in the case of YSZ columnar microstructure samples appeared to be very sensitive to small changes in microstructure and surface topography, it was decided to apply the additional surface treatment in order to improve their hydrophobicity. The radio-frequency (RF) plasma jet with hexamethyldisiloxane (HMDSO) admixture was used for this purpose. After such hydrophobization, the wetting behavior of the A3-D and A3-P YSZ samples turned from hydrophobic/hydrophilic up to the superhydrophobic state, i.e., from 129 ± 3° up to 150 ± 2° (for A3-D YSZ) and from 14 ± 7° up to 151 ± 1° (for A3-P YSZ).

The phenomenon of wettability transition is connected to the simultaneous modification of the surface chemistry ensured by the deposition of the nanostructured layer of hydrophobic organosilicons with multi-scale topography [24]. The deposited layer was composed of irregular-shaped nano-sized particles (~100 nm in size) and their agglomerates (~1-2 µm in size) possessing dendritic morphology. The valleys/pores in the dendritic structure created a space for air-pockets to be entrapped, thereby resulting in enhanced superhydrophobic behavior.

To estimate the robustness of the superhydrophobic behavior, the WSP-H YSZ, A3-D modified and A3-P modified samples were subjected to the water-flush test for ~5 min using tap water [12]. The superhydrophobic behavior of each YSZ sample was partially or completely degraded after this brief test, resulting in a loss of water mobility.

One of the potential applications of the YSZ coating with superhydrophobic behavior is in the anti-icing surfaces for airplanes and wind turbines where a high water contact angle and a relatively low density of YSZ (~2 g/cm^3) material would be beneficial. However, even though the superhydrophobic state was obtained, such a thin layer with dendritic structure composed from nano-particles was not expected to be wear-resistant or useful in sacrificial applications. Thus, further research focused on the production of wear-resistant coatings with multi-scale topography produced by the means of high-velocity oxy-fuel spraying.

5.3 Wetting behavior of WC-Co-Cr cermet coatings produced by high-velocity oxy-fuel spraying

The previous research discovered that the porosity of WC-Co-Cr thermal sprayed coatings had a significant impact on wetting behavior. Therefore, in order to lower porosity, and because of other advantages such as the higher hardness of coatings, higher efficiency and mobility, high-velocity oxy-fuel spraying (HVOF) technology was chosen. The WC-Co-Cr coatings were obtained from three different powders: (i) coarse powder (C16 sample), (ii) coarse powder with ultra-fine WC particles (CU16 sample) and (iii) fine powder with ultra-fine WC particles (CU31 sample). The main idea was to fabricate hard and wear-resistant coatings with a multi-scale surface topography, which could result in hydrophobic or superhydrophobic behavior. Additionally, Si-oil modification was applied (i) to isolate the surface roughness effect on wetting behavior and (ii) to amplify the hydrophobicity of the coatings.

The EDX analysis revealed the presence of W, C, O, Co and Cr elements that were from the base material, while the analysis of the modified samples showed the presence of an additional Si element (~10 wt. %) that was supposed to be from Si-oil modification. The distribution of elements was similar for all studied coatings.

A comparative XRD analysis of unmodified as-sprayed WC-Co-Cr coatings showed clear peaks of WC, W_2C and W phases, while no peaks of Cr and Co binders were observed. The XRD patterns were similar for the C16 and CU16 coatings with nearly equal intensities of WC, W_2C and W phases, but distinctly different from the CU31 coating, as clearly seen from Rietveld refinement, Table 2.

Table 2 Crystalline phases and crystallinity content in C16, CU16 and CU31 as-sprayed coatings

Coating	Phase content [wt.%]			Crystallinity content [%]
	WC	W_2C	W	
C16	51	37	12	36
CU16	49	39	12	41
CU31	20	54	26	50

The quantitative XPS analysis of polished unmodified samples revealed that the surface chemistry of the cermet coatings was represented mainly through compositions of W (W 4f), O (O 1s) and C (C 1s). Clear peaks of Co 2p and Cr 2p were not detected. The deconvolution of C 1s high-resolution spectra revealed a very similar result with the central peak at ~283 eV addressed to the W-C composition. Only the CU31 sample had the second smaller peak at ~285 eV that was supposed to be related to the hydrocarbon C-H compound.

All the coatings were of a lamellar or splat-like microstructure that is very common for HVOF deposits [25-30]. The porosity of HVOF deposits was much lower when compared with plasma sprayed WC-Co-Cr coatings, i.e., C16 and CU16 had ~1.5% and CU31 had ~1% of porosity.

The topographic analysis was performed on as-sprayed, as-sprayed modified and polished unmodified coatings. In the case of the polished unmodified surfaces, topography measurements were done to ensure that the root mean square height *Sq* was below 0.20 μm and the surface roughness factor *Rs* was below 1.01. All of the studied coatings showed the presence of the multi-scale roughness, i.e. a large-scale (tens of microns) wavy surface connected to the spraying process [31] with micron-sized (approximately from 2 to 10 microns) peaks and valleys that were covered by ultra-fine WC carbide particles (hundreds of nanometers in size). Such a unique multi-scale roughness was connected to the agglomerated and sintered initial feedstock powder with ultra-fine WC particles that created nano-scale topographical features on the surface of micron-sized splats.

The measured roughness parameters of the C16, CU16 and CU31 coatings are summarized in Table 3.

Table 3 Roughness parameters of surfaces of C16, CU16 and CU31 as-sprayed unmodified coatings

Coating	Sa [μm]	Sq [μm]	Ssk [-]	Sku [-]	Rs [-]
C16-AS	3.8	4.9	0.21	4.35	2.13
CU16-AS	5.4	6.7	0.18	3.03	2.23
CU31-AS	6.8	8.3	0.04	2.56	1.92

The results of the measurements of water contact angle (WCA), surface free energy (SFE) and distribution of its components are presented in Table 4. Following the XPS quantitative analysis results, the surface chemistry of the C16, CU16 and CU31 samples was represented by polar W-O oxides and polar W-C carbides, providing hydrophilic behavior due to the polar-polar interaction with water. The only difference was found in the deconvoluted C 1s spectra of the CU31 sample, revealing the presence of an additional small peak at ~285 eV that was addressed to the C-H compound. Recent studies have already reported [32, 33] on the effect of non-polar hydrocarbons on hydrophobic behavior. Therefore, it could explain the presence of additional C-H peak in deconvoluted C 1s spectra of the CU31 sample.

The analysis of the WCA of the as-sprayed unmodified C16, CU16 and CU31 coatings, Table 5. To the best of the author's knowledge, this was the first report on WC-Co-Cr cermet HVOF sprayed coating with a WCA value above 140° in the as-sprayed state. The Si-oil surface modification amplified hydrophobicity up to the superhydrophobic state with a very low sliding angle (SA) and SFE values for all the studied coatings, as listed in Table 5. The best water repellency and mobility performance was found on the C16 and CU16 coatings with a WCA > 170° and a SA of 8° and 5°, respectively. Ultra-fine WC carbide particles embedded into the Co-Cr metallic matrix formed nano- and submicron-sized peaks, see Figure 4. These micron-scale peaks covered by nano-scale peaks and valleys/pores enlarged the total surface area, providing more space for air-pockets to be entrapped, improving hydrophobic behavior. According to the combined Wenzel-Cassie-Baxter wetting regime, hydrophobicity increases with an increasing surface roughness factor *Rs*. Thereby, the higher hydrophobicity of the as-sprayed and as-sprayed modified C16 (*Rs* = 2.13) and CU16 (*Rs* = 2.23) coatings was promoted by a higher surface roughness factor *Rs*, Table 3. Using Eq. 4 for the combined regime of wetting, the calculated f_s values were 4.1% for the C16, 3.8% for the CU16 and 23.1% for the CU31 in the as-sprayed modified conditions. Thus, 95.9% (for the C16), 96.2% (for the CU16) and 76.9% (for the CU31) area of the water droplet was related, in fact, to the liquid-gas (air) contact, providing a high water repellency and mobility.

Table 4 Water contact angle and surface free energy values of the polished and polished modified C16, CU16 and CU31 coatings

Sample	State	WCA [°]	SFE [mJ/m²]	γ^d [mJ/m²]	γ^p [mJ/m²]	γ^p/SFE
C16	P	55 ± 1	50.26	35.71	14.55	0.29
	P-M	107 ± 2	27.05	27.00	0.05	<0.01
CU16	P	53 ± 2	51.30	36.46	14.84	0.29
	P-M	106 ± 1	27.76	28.73	0.03	<0.01
CU31	P	68 ± 1	46.58	37.36	9.23	0.20
	P-M	105 ± 2	28.21	28.16	0.05	<0.01

Table 5 Water contact angle, sliding angle and surface free energy values of the as-spayed and as-sprayed modified C16, CU16 and CU31 coatings

Sample	State	WCA [°]	Sliding angle [°]	SFE [mJ/m²]
C16	AS	122 ± 3	-	17.37
	AS-M	>170	8	2.08
CU16	AS	143 ± 2	-	12.79
	AS-M	>170	5	2.10
CU31	AS	88 ± 2	-	28.49
	AS-M	152 ± 4	10	2.85

These experiments showed that using the agglomerated and sintered WC-Co-Cr powder feedstock in HVOF spraying enables the deposition of coatings with a multi-scale surface roughness, leading to the hydrophobic behavior in the as-sprayed state and the superhydrophobic behavior in the as-sprayed modified state. In both the as-sprayed and as-sprayed modified states, the highest water repellency and water mobility were observed in the CU16 coating (the WCA was close to 150° in the as-sprayed state; WCA > 170° and SA ~ 5° in the as-sprayed modified state) fabricated from bi-modal powder feedstock (coarse powder with ultra-fine WC particles). Therefore, using bi-modal powder feedstock can ensure the optimal surface topography with a high water repellency.

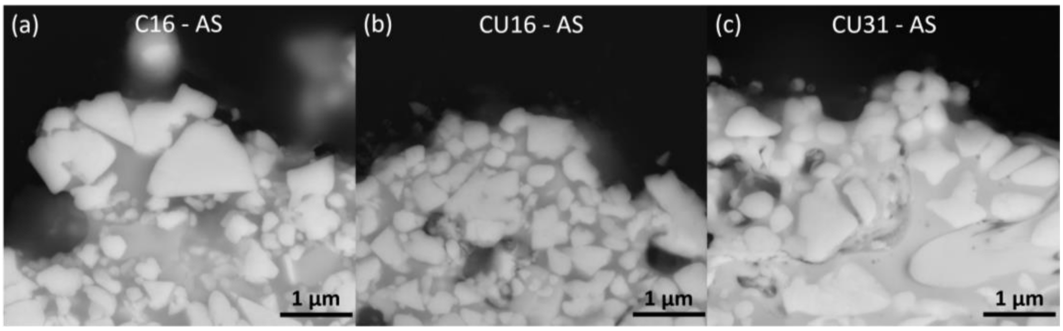

Figure 4 Cross-sections of the as-sprayed (a) C16, (b) CU16 and (c) CU31 coatings' top part with WC carbides (white color) embedded into Co-Cr metallic matrix (light gray color)

5.4 Mechanical properties, wear/erosion resistance and non-destructive durability tests of hydrophobic WC-Co-Cr coatings

The mechanical properties of the WC-Co-Cr HVOF as-sprayed C16, CU16 and CU31 coatings were evaluated using the Vickers microhardness test at samples cross-sections. The highest microhardness was measured for the CU16 coating (1155 ± 112 HV) and nearly equal values were measured for the CU31 and C16 coatings (988 ± 66 HV and 966 ± 119 HV, respectively).

For the cavitation erosion (CE) resistance test, the two most hydrophobic C16 and CU16 samples in the as-sprayed and as-sprayed modified states were selected. The as-sprayed modified samples were tested for 20 minutes, and the test was terminated once the superhydrophobic effect was lost. The WCA value decreased down to ~140-145° and was associated with the gradual removal of the Si-oil modification layer. The mass loss after 20 minutes of testing was ~0.01 g in both samples. The as-sprayed unmodified C16 and CU16 samples were tested for 165 min and 120 min, respectively, and stopped once the loss of hydrophobicity was observed. The C16 sample produced from coarse powder revealed a higher resistance to cavitation erosion with a cumulative mass loss of 0.030 (after 120 min) and 0.042 g (after 165 min). On the other hand, the CU16 sample produced from bi-modal powder (coarse powder with ultra-fine WC particles) had a cumulative mass loss of 0.040 g already after 120 min of testing. Even though the eroded surfaces of the C16 and CU16 samples were relatively rough after the CE test, the hydrophobic behavior was lost due to the formation of cracks within the coatings.

As for the CE test, the two most hydrophobic as-sprayed and as-sprayed modified C16 and CU16 samples were selected for the Slurry Abrasion Response (SAR) test. The superhydrophobicity of the as-sprayed modified C16 and CU16 samples was capable of withstanding erosion wear for 48 cycles (1 minute of testing), with a decrease in WCA value down to 140-145°. Additional re-covering of the experimental coatings by Si-oil restored superhydrophobic behavior, resulting in a very high WCA of about 170°. According to author's knowledge, there are no reports evaluating the robustness of the hydrophobic/superhydrophobic coatings utilizing SAR test. Hydrophobic as-sprayed C16 and CU16 samples were tested for 17 280 cycles (6 hours of testing). The changes in surface topography and WCA values were recorded after 4 and 6 hours of testing, as it was found to be the period in which the wetting behavior switched from hydrophobic to hydrophilic. Even though the hydrophilic behavior was observed in both the C16 and CU16 as-sprayed samples, there were still parts of the coatings' surfaces that showed hydrophobic behavior even after 6 hours of testing. The WCA values decreased from ~122° to ~118° (after 4 hours) and ~70° (after 6 hours) for the C16 sample, and from ~143° to ~128° (after 4 hours) and ~74° (after 6 hours) for the CU16 sample. This result proves the sufficient robustness of the hydrophobic wetting behavior of WC-Co-Cr coatings that could withstand 11 520 cycles and partially remained, even after 17 280 cycles of sacrificial testing.

Evaluation of the icephobic behavior was carried out on superhydrophobic as-sprayed modified C16/CU16 samples, hydrophobic as-sprayed and polished modified C16/CU16 samples. Conventional materials, such as aluminum and stainless-steel, were analyzed as well to provide a comparison, see Figure 5. The aluminum and stainless-steel substrates were in the ground state with a surface arithmetic mean height *Sa* of ~1.2 µm, and the measured WCA values were of ~68° and ~71° respectively. Considering that the ice adhesion strength decreases with an increasing WCA value [34], it can be concluded that the C16/CU16 as-sprayed modified coatings possess a significantly improved icephobicity in comparison to unmodified coatings and conventional construction materials.

For the acid-phobic test, a droplet of the mixture of concentrated sulfuric acid in water (4.7 M, 9.3 M and 14 M) and pure concentrated sulfuric acid were deposited on the surface of the C16/CU16 as-sprayed modified and the C16/CU16 as-sprayed coatings. The results are summarized in Table 6. In recent studies [35], it was reported on the importance of increasing the corrosion-resistance of WC-based cermet coatings due to the corrosive nature of their service environments. This short-term test demonstrates the potential of Si-oil surface treatment to improve corrosion resistance and increase the service lifetime of the WC-Co-Cr coatings.

During the self-cleaning test, the water droplets were quickly rolling off the tilted surface of the C16/CU16 AS-M coatings, collecting the alumina dust and producing clean lines on the coatings surface, Figure 6a. As demonstrated in Figure 6b, the continuous flow of muddy water with suspended ultra-fine WC particles was sent onto the tilted surface of the C16/CU16-AS-M coating and quickly rolled off without any apparent contamination remained.

These preliminary observations pointed out a promising durability of superhydrophobicity of WC-Co-Cr C16/CU16 AS-M coatings against powder/slurry contaminations.

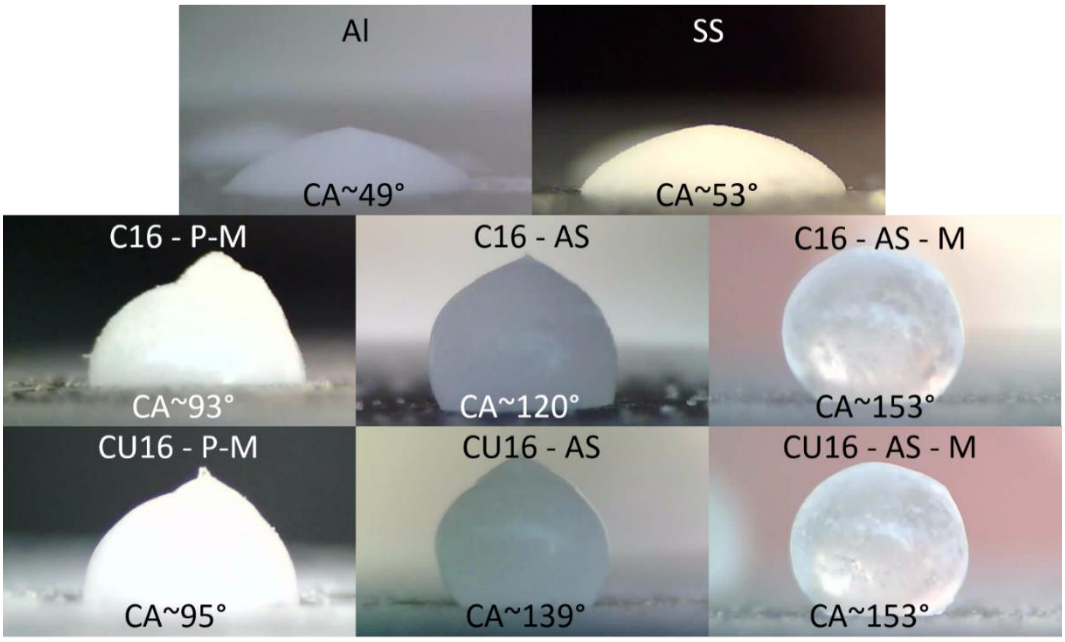

Figure 5 Icephobic behavior of Al/SS substrates and C16/CU16 coatings

Table 6 Concentrated sulfuric acid and its water-mixtures contact angle values of C16/CU16 coatings

Sample	H_2SO_4 in water mixture CA [°]			H_2SO_4 CA [°]
	4.7 M	9.3 M	14 M	
C16 AS	23 ± 2	20 ± 3	19 ± 1	2 ± 2
C16 AS-M	153 ± 1	153 ± 1	148 ± 3	4 ± 1
CU16 AS	25 ± 1	21 ± 3	20 ± 3	2 ± 2
CU16 AS-M	153 ± 2	153 ± 1	149 ± 2	5 ± 2

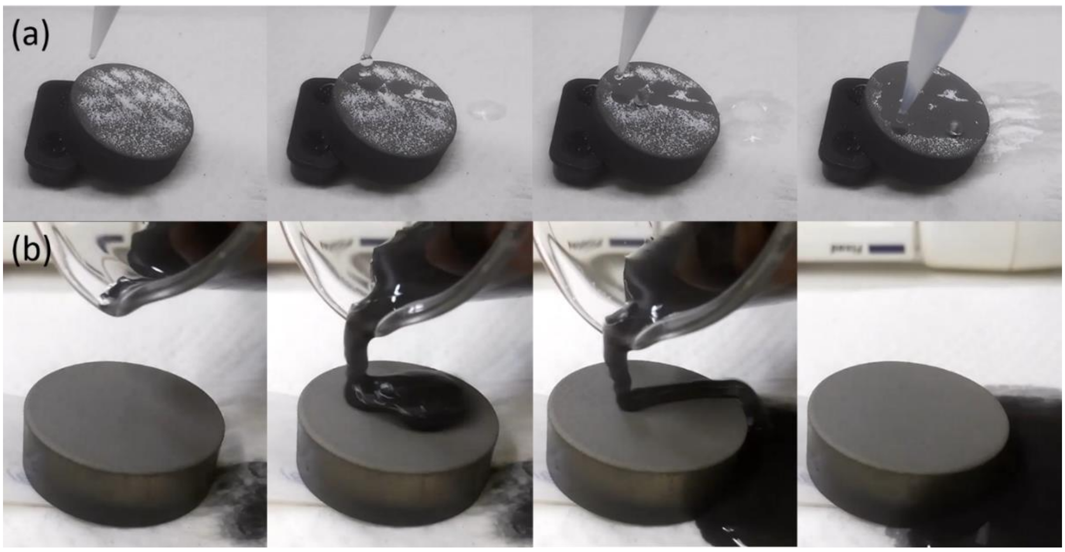

Figure 6 Representation of (a) self-cleaning and (b) muddy-water transportation tests

6 Conclusions

The main aim of the thesis was to produce the wear-resistant coatings with hydrophilic/hydrophobic behavior by means of thermal spraying; to perform a detailed analysis of produced coatings in order to assess the interconnections between microstructure, surface chemistry and surface topography with their wetting behavior; and to estimate the properties and robustness of the wetting behavior of produced coatings.

In the first part of the experimental work, several wear-resistant ceramic and cermet coatings, namely ZrO_2-Y_2O_3, Al_2O_3, Cr_2O_3-SiO_2-TiO_2 and WC-Co-Cr, were produced by means of atmospheric plasma spraying. All the coatings showed hydrophilic behavior with the Wenzel wetting regime due to the presence of pores/cracks present in the coatings, which resulted in a gradual infiltration of the water droplets into the coatings. The effect of the coatings porosity and/or cracks on the wetting behavior was crucial and, therefore, the influence of surface topography on wetting behavior remained unclear.

In the second part, the YSZ coatings were produced using liquid and solid feedstocks in order to understand the effect of microstructure on wetting behavior. Four series of samples were produced, namely YSZ coatings with a lamellar microstructure (employing the F4 plasma torch) and with a columnar microstructure (employing the WSP-H and Axial III plasma torches). The comparative analysis of microstructure, surface chemistry and surface topography and their effect on wetting behavior revealed that (i) the YSZ coating with lamellar microstructure (the F4 YSZ coating) promoted hydrophilic behavior with the Wenzel wetting state due to the infiltration of the water into the pores and cracks in the coating; (ii) the presence of pores in the columnar microstructure located between the flat columns promoted almost superhydrophilic behavior with the Wenzel wetting state in the A3-P YSZ coating; (iii) the denser flat columnar microstructure of the A3-D YSZ coating prevented the penetration of water into the coating, resulting in hydrophobic behavior with the Cassie-Baxter wetting state; and (iv) the rough surface of the columns, as well as the high surface area, of the WSP-H YSZ sample provided superhydrophobic behavior with the Cassie-Baxter wetting state. With the aim to overcome the dependency of wetting behavior on microstructural and topographical features of YSZ coatings, the additional RF-plasma jet surface treatment was made. Such a layer provided transition of wetting behavior from hydrophilic (A3-P YSZ sample) and hydrophobic (A3-D YSZ sample) states to superhydrophobic one. Nevertheless, the superhydrophobic behavior with high water mobility of the as-sprayed WSP-H and modified A3-D/A3-P YSZ samples was not able to withstand the short-term water-flush test pointing out the need for further research on fabrication of water-repellent wear-resistant coatings.

The third part of the experimental work aimed to fabricate wear-resistant coatings from WC-Co-Cr cermet materials using three different powder feedstocks, by the means of high-velocity oxy-fuel spraying. The coarse powder, a coarse powder with ultra-fine WC particles and a fine powder with ultra-fine WC particles were used in order to deposit coatings with multi-scale topography. To understand the influence of surface topography and surface chemistry on wetting behavior, all the coatings were studied in the as-sprayed, polished (isolated effect of surface chemistry), as-sprayed modified (isolated effect of surface topography) and polished modified states. A technologically simple way to improve surface hydrophobicity based on a Si-oil treatment was provided. All cermet coatings were hydrophilic in the polished state, but hydrophobic and almost superhydrophobic in the as-sprayed state. Additional surface modification provided by a Si-oil turned wetting behavior into the superhydrophobic state of all cermet coatings. The highest water contact angle value (WCA ~ 143° in the as-sprayed; WCA > 170° in the as-sprayed modified) and the lowest sliding angle (SA ~ 5°) was found for the CU16 coating in the as-sprayed and as-sprayed modified states. The CU16 coating was produced from a coarse powder with ultra-fine WC particles, revealing that such a combination provided an optimal multi-scale surface topography for water repellency and water mobility.

Finally, in the last experimental part, the mechanical properties of cermet coatings and the robustness of hydrophobic/superhydrophobic behavior were evaluated by microhardness measurements, cavitation erosion, slurry abrasion response and unconventional non-destructive tests. The highest microhardness was measured for the CU16 coating produced from the coarse powder with ultra-fine WC particles. The superhydrophobic behavior of experimental samples was lost after 20 min of the cavitation erosion test and after 48 cycles of the slurry abrasion response test. The robustness of the hydrophobic behavior of cermet coatings was able to withstand cavitation for almost three hours (165 min); 11 520 cycles (4 hours) and partially remained after 17 280 cycles (6 hours) of slurry abrasion testing. These results showed that the hydrophobicity of the cermet coatings was robust enough even for demanding sacrificial industrial applications. Non-destructive tests on the icephobic, acid-phobic, self-cleaning and muddy-water transportation performance of the superhydrophobic C16 and CU16 coatings were carried out. The icephobic performance showed that C16 and CU16 as-sprayed modified coatings can significantly increase the icephobicity of conventional construction materials. The acid-phobic test demonstrated the potential of the Si-oil surface treatment to improve of corrosion resistance and increase the service lifetime of the WC-Co-Cr coatings. The self-cleaning and muddy-water transportation tests also revealed good results, with no apparent contamination or negligible wear of the superhydrophobic layer.

7 Bibliography

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8 Summary of author's activities

Publications related to the thesis

[1] **P. KOMAROV**, D. JECH, S. TKACHENKO, K. SLÁMEČKA, K. DVOŘÁK, L. ČELKO. Wetting behavior of wear-resistant WC-Co-Cr cermet coatings produced by HVOF: The role of chemical composition and surface roughness. *Journal of Thermal Spray Technology*. 2021, **30**(1–2), 285–303. doi:10.1007/S11666-020-01130-6

[2] **P. KOMAROV**, D. JECH, L. ČELKO, B. PIJÁKOVÁ, D. ZHOU, R. VASSEN. Influence of RF plasma jet surface treatment on wetting behavior of yttria stabilized zirconia SPS coatings. *Defect and Diffusion Forum*. 2020, **405**, 423–429. doi:10.4028/www.scientific.net/DDF.405.423

[3] **P. KOMAROV**, L. ČELKO, M. REMEŠOVÁ, K. SKOROKHOD, D. JECH, L. KLAKURKOVÁ, K. SLÁMEČKA, R. MUŠÁLEK. The role of microstructure on wettability of plasma sprayed yttria stabilized zirconia coatings, in: *Metal 2017 - 26th Int. Conf. Metall. Mater.*, TANGER Ltd, 2017: pp. 1116–1121.

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Other publications

[1] L. ČELKO, S. TKACHENKO, M. CASAS-LUNA, L. DYČKOVÁ, V. BEDNAŘÍKOVÁ, M. REMEŠOVÁ, **P. KOMAROV**, A. DEÁK, M. BALÁŽ, D. CRAWFORD, S. DIAZ-DE-LA-TORRE, E. BODOKI, J. CIHLÁŘ. High-energy ball milling and spark plasma sintering of molybdenum - lanthanum oxide (Mo-La_2O_3) and molybdenum – lanthanum zirconate (Mo-$La_2Zr_2O_7$) composite powders. *International Journal of Refractory Metals and Hard Materials*. 2022, **102**, 105717. doi:10.1016/j.ijrmhm.2021.105717

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[4] Z. PAVLOUŠKOVÁ, D. JECH, **P. KOMAROV**, I. ROČŇÁKOVÁ, L. DYČKOVÁ, M. REMEŠOVÁ, L. ČELKO, D. HOLEMÝ. Characterization of high-speed alumina abrasive grinding wheel. *Defect and Diffusion Forum*. 2020, **405**, 365–369. doi:10.4028/ www.scientific.net /DDF.405.365

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[7] L. DYČKOVÁ, **P. KOMAROV**, M. REMEŠOVÁ, M. DYČKA, K. DVOŘÁK, M. MENELAOU, L. ČELKO. Optimization of molybdenum powder milling parameters. *Metal Working and Material Science*. 2018, **20**(3), 109–122. doi:10.17212/1994-6309-2018-20.3-109-122

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[9] D. JECH, L. ČELKO, **P. KOMAROV**, J. ZIEGELHEIM, Z. ČESÁNEK, J. SCHUBERT. The role of different atmospheric plasma spray parameters on microstructure of abradable AlSi-polyester coatings. *Solid State Phenomena*. 2017, **270**, 224–229. doi:10.4028/ www.scientific.net /SSP.270.224

[10] L. ČELKO, D. JECH, **P. KOMAROV**, M. REMEŠOVÁ, K. DVOŘÁK, I. ŠULÁK, B. SMETANA, K. OBRTLÍK. Failure mechanism of yttria stabilized zirconia atmospheric plasma sprayed thermal barrier coatings subjected to calcia-magnesia-alumino-silicate environmental attack. *Solid State Phenomena*. 2017, **270**, 39–44. doi:10.4028/ www.scientific.net /SSP.270.39

Product

- Co-author of the functional sample “Plošný vyhřívací povlak s vysokou homogenitou teplotního pole” (Surface heating coating with high temperature field homogeneity)

Internships, conferences and trainings

- 2-month internship (September - November 2018) at the department of Materials for High-Temperature Technologies of the Forschungszentrum Jülich (Germany) under the supervision of Prof. Dr. Robert Vaßen
- 2-month internship (July – August 2018) at the department of Materials Science and Technology of Materials of the Novosibirsk State Technical University (Russia) under the supervision of Prof. Dr. Vladimir Bataev
- 2-month internship (July – August 2017) at the department of Materials Science and Technology of Materials of the Novosibirsk State Technical University (Russia) under the supervision of Prof. Dr. Vladimir Bataev

- COMAT 2020, Pilsen, Czech Republic
- 9 RIPT 2019, Jülich, Germany
- M&F 2019, Nový Smokovec, Slovakia
- 14th CCMPPS 2017, Mariánské Lázně, Czech Republic
- METAL 2017, Brno, Czech Republic

- Workshop on “The evolution of TBC with emerging thermal spray technologies” (April 2018, Pilsen, Czech Republic)
- Applied-seminar “Modern measurement techniques for surface chemistry” (May 2018, Filderstadt, Germany)

- Core facilities self-user for SEM, EDX, XRD, XPS, WCA/SFE, metallographic samples preparation

Participation in research projects

- Specific Research Project CEITEC VUT-J-19-5799 (VUT-junior project 2019) “Thermal spraying as a promising way to develop hydrophobic coatings from WC material”