Review Report on PhD Thesis

Faculty: **Central European Institute of Technology** Academic year: **2021/2022**

Brno University of Technology in Brno

Student: **Pavel Komarov**

Doctoral study program: **Advanced Materials and Nanosciences**

Field of study: **Advanced nanotechnologies and microtechnologies**

Supervisor: **doc. Ing. Ladislav Čelko, Ph.D.**

Reviewer**:** **Prof. Lech Pawłowski**

PhD thesis title**: Advanced hydrophobic and hydrophilic surface treatments for non-nuclear energetics**

Topicality of doctoral thesis:

The thesis of Pavel Komarov deals with the problem of wettability of thermally sprayed coatings. The wettability is associated with other mechanical properties such as wear and erosion resistance. Moreover, the wettability is tested for water, ice, sulfuric acid being more or less concentrated and for water with alumina dust. The author tested oxide ceramics such as ZrO_2+Y_2O_3 (YSZ), Al_2O_3, Cr_2O_3+SiO_2+TiO_2 and cermet of WC carbide with Co+Cr. These materials were used as dry powder and liquid suspension feedstock of two thermal spraying technique, namely atmospheric plasma spraying (APS) and high velocity oxy-fuel (HVOF) deposition.

Three different APS processes were applied using torches having: (i) one cathode and radial injection (F4); (ii) three cathodes and axial injection (Axial III), and; (iii) water stabilized plasma jet (WSP). The sprayed coatings's surfaces were tested as: (i) as-sprayed; (ii) ground and polished; and (iii) post-spray treated using injection of hydrophobic agents. The chemical composition of obtained coatings were characterized using energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS).Their crystal phases were identified using X-ray diffraction (XRD). The wettability were testes by water contact angle (WCA) measurements and interpreted by coatings' surface roughness and microstructure. Finally, the wettability models of *Wenzel* and *Cassie-Baxter* were used to interpret the obtained WCA values.

Meeting the goals set:

The goal of the thesis was defined in page 32 as follows: „to develop a technology to fabricate wear-resistant hydrophobic/hydrophilic coatings employing thermal spraying process". The goal is very general and the author added nine detailed steps to reach it. As the goal was broad, it would be more useful to find a couple practical application of thermally sprayed deposit in which the wettability and/or interaction of coating's surface with water plays an essential role. Having such application, the author could have defined specifications to be reached. Moreover, the title of thesis indicates the "non-nuclear energetics" but its content does not go into the details of this application.

On the other hand, the goal was reached and the author tested carefully wettability, wear resistance of numerous ceramic and cermet coating sprayed using different methods, and interpreted obtained results with the models available in the literature.

Problem solving and dissertation results:

The author started to correlate the wettability with chemical composition and chemical bonds resulting in, well known in thermodynamics, surface energy. Following this correlation, the low surface energy result in high WCA and the polar bonds of ceramics are similar to polar bond of water resulting in hydrophilicity of surface of ideally smooth surface following the *Owens-Wendt* theory. As the real materials have rough surfaces, it was necessary to add the surface roughness and the models of: (i) *Wenzel* stating that roughness amplifies the behavior of smooth surface; and, (ii) *Cassie-Baxter,* which interprets roughness as adding the air pockets and reducing the contact of liquid with the surface. These models were interpreted in view of important characteristics of thermally sprayed deposits namely: (i) open porosity, which enables liquid on the surface to be absorbed; (ii) lamellar or columnar microstructure resulting from size of powder used in the feedstocks, which influences the roughness; and, (iii) surface chemistry modified by post-spray addition of organic liquids promoting hydrophobicity.

The tests of ceramic and cermet deposits obtained using APS made for as sprayed, ground and polished samples indicated the hydrophilic behavior with the WCAs lower than 90°. The as-sprayed coatings had the greatest WCA what indicates the applicability of *Cassie-Baxter* model. The cracks and open porosity inside the coatings result in the reduction the WCA with as water is absorbed by coatings. Consequently, the YSZ with different microstructure obtained with different plasma torches was selected to be studied in more details. The results of wettability did show very different behavior, namely hydrophilic for lamellar microstructure and hydrophobic for columnar one.

The cermet coatings of WC+Co+Cr sprayed using HVOF torch using different powders was also tested. The coatings were hydrophilic after polishing and the difference in the WCA resulted from different degree of WC decomposition at spraying. The as-sprayed coatings were more hydrophobic and the model of *Cassie-Baxter* could be applied to explain their behavior in contact with water droplets. Some of wear resistance tests, namely slurry abrasion one, did modify the wettability of coating from hydrophobic to hydrophilic. In general, the cermet coatings preserved their hydrophobicity in as-sprayed state after the wear tests.

Importance for practice or development of the discipline:

The study of wettability is of practical importance in many applications starting from bio-fouling important for ships up to corrosion resistance important with the parts being in contact with water environment. The thermal spraying processes enable relatively cheap deposition of all type of materials and a systematic study of wettability of surfaces of coating obtained using different techniques is important. The reviewed PhD studies oxide ceramics obtained by APS and cermet with carbide obtained by HVOF. The study can be followed for the particular applications in which wettability plays an important role. Moreover, the cheap technique of cold spraying can be included in the cermet coatings manufacturing.

Formal adjustment of the thesis and language level:

The PhD is well organized and reviews correctly the available literature including 122 references of the treated subject. The theory concerning wettability is also show and well explained. Moreover, the subject of the thesis is developed in 4 papers published in the reviewed journals with the participation of Pavel Komarov as the first author.

The English language of the thesis is understandable and clear. The list of abbreviations helps in the lecture of thesis. It would be useful to separate this list with the list of symbols used in equations and tables.

Questions and comments:

- Whether thermal spraying of composites including polymers can be useful technology to be developed for coatings with hydrophobic surface? Which polymer and which spray technique can be recommended?
- The corona treatment of polymers is used industrially to modify their surface and render possible printing. Can this technique be useful as the post-spray treatment and for which type of coatings?
- Do you think that the impregnation of the sprayed coatings surface with thermally cured polymer is a useful solution for post-spray treatment?
- As the wettability models of *Wenzel* or *Cassie-Baxter* are not entirely applicable for thermal spray deposits having open porosity and vertical cracks, would it be useful to develop the model, which is better adapted to the coatings' microstructure?
- The use of XPS technique to characterize the chemical composition of the coatings is useful but limited to the coatings' surface and it is necessary to decontaminate very carefully tested samples.
- The title of the thesis indicated non-nuclear energetics. Please precise which application you have in mind and specify more precisely the requirement concerning wettability for this application.

Conclusion:

In my opinion, the reviewed thesis fulfills all requirements posed on theses aimed for obtaining PhD degree. This thesis is ready to be defended orally, in front of respective committee.

In Couzeix, date 11 February 2022

Prof. Lech Pawłowski

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