Fraunhofer IWS

Dr. Filofteia-Laura Toma
Senior Engineer Scientist
Fraunhofer Institute for Material and Beam Technology IWS
Winterbergstrasse 28, D-01277 Dresden, Germany

Report on the Doctoral Thesis entitled

Advanced Plasma-Sprayed Ceramic Coatings Prepared from Liquid Feedstocks

written by

Ing. Tomáŝ Tesař

submitted to

Czech Technical University in Prague, Faculty of Nuclear Sciences and Physical Engineering

<u>Topic and relevance</u>

The Doctoral Thesis submitted by Mr. Tesař comprises of seven chapters, followed by References list and an appendix with authors' publications lists, spanning 108 pages in total. The topic of the thesis is based on four peer-reviewed papers submitted in international, well-impacted journals with Mr. Tesař as first author and main investigator. It is worthy to notice, that Mr. Tesař is co-author of ten peer-reviewed papers which are not directly related to the thesis. This denotes his high interest for different aspects of suspension and solution spraying, but unfortunately it cannot be established what was the personal contribution of Mr. Tesař in these publications. A more detailed discussion in the Section 5.5 would have been advantageous. References list contained only 78 citations which in reviewer's opinion is quite short for a PhD Thesis.

Thermal spraying with liquid feedstocks is a new emerging technology showing currently an increasing interest and high relevance for both scientific community and industry. With liquid thermal spraying, tailored coatings with desired properties can be achieved and thus new applications of these coatings are expected. Nonetheless there is still great need in the development of cost-effective, functional coatings with high deposition efficiency by means of liquid thermal spraying. Mr. Tesař focuses the work of his thesis on alumina and chromia-doped alumina coatings obtained by means of intermixing suspensions of fine powders, intermixing of solutions precursors and using a new concept of hybrid spraying by simultaneous deposition of suspensions and dry coarse powders, aiming to functional coatings with increase content of α-Al_2O_3 phase. Efforts have been devoted in the understanding of parameters affecting the liquid-plasma interaction, coating built-up mechanisms and finally the coating properties and their functional performances.

In the first part of the thesis, the current state-of-the-art of the plasma spraying with spray powders and liquid feedstocks, as well the plasma-jet-liquid interactions were briefly described. An inert carrier gas (Ar, N_2) is used to feed the spray powders in the plasma jet; using air or Ar+H_2 (Section 1.3) can result in the chemical modification or reactions of sensitive spray powders. With liquid feedstocks very fine raw powders (from nanometers to several micrometers) can be fed in the plasma; the formulation of an appropriate suspension or solutions suitable for spraying is one of the major key parameters in the liquid spraying, which needed to be more extensively described. Recent literature related to different aspects in the development of suspensions / solutions could not be found in the thesis. Al_2O_3 is one of the most studied materials in the literature, but the literature study for both conventional and suspension-sprayed Al_2O_3-based coatings is here very limited.

Methods

The hybrid water-stabilized plasma (WSP) torch, developed at the Institute for Plasma Physics in Prague was used to spray both the powders and liquid feedstocks; this is a new approach when compared to the gas-stabilized plasma torches, which are mainly employed to produce SPS and SPPS coatings. During coating spraying, the substrate temperature was continuously monitored. For mostly of the spray trials, shadowgraphy imaging was used as tool to visualize and to optimize the liquid penetration into the plasma jet.

Commercial available ready-to-spray suspensions and in-house-made water- and ethanol-based suspensions/solutions precursors were employed as liquid feedstocks. The liquid feedstocks were fed into the plasma jet from a custom-built pressure-based liquid feeder. The effects of particles sizes, solid content / concentration of the precursor, liquid media, and presence of the stabilizers on the properties of the suspensions / solutions were evaluated. The feedstocks were characterized in terms of sedimentation evolution with time and viscosity measurements at different shear rates. The reviewer missed measurements and results concerning the particle sizes distribution, pH value, Zeta-potential, which are mandatory for suspension development.

The microstructure of the sprayed coatings was characterized in metallographically prepared cross-section and top surfaces (free surfaces) using optical microscopy and SEM. Image analysis was used to determine the porosity. Phase and chemical compositions were evaluated by XRD and NMR. Chemical analysis of alumina-chromia coatings was analyzed by means of XRF. For selected coatings Vickers hardness, tensile adhesion strength and wear resistance tests were used to evaluate their mechanical properties. Thermochromic behavior of alumina-chromia coatings obtained from solutions precursors during heating-cooling cycling was monitored by temperature-resolved colorimetry. Because one of the goal of the thesis was to produce Al_2O_3 with high content of corundum phase (α-Al_2O_3), measurements of the electrical / insulating properties of the sprayed coatings, as well as the corrosion resistance were highly expected.

Goal achievement

The main objective of the thesis is a contribution to the development of the alumina-based coatings with high content of corundum, low porosity and high deposition rate, as well as in the understanding of the coating buildup via liquid spraying. The microstructural features of the coatings could be correlated to the feedstock formulation. Contrary to expectation, i.e. coatings prepared by GPS-torches, dense alumina coating with outstanding mechanical properties was prepared from a custom-made ethanol-based suspension, whereas extremely porous and soft coating with high fraction of α-phase resulted from solution precursor (Paper I). Using three different suspensions in terms of particle sizes, solid material and content, solvent Mr. Tesař emphasized the key role of the atomization of the suspension which determines the final size of the impinging melt particles (Paper II). However the suspension atomization in the plasma jet is strongly influenced by suspension characteristics i.e. material, solid content, solvent, viscosity, surface tension, or latent heat. Unfortunately Mr. Tesař does not provide a discussion regarding the relationship of the suspension properties on the interaction plasma jet – suspension.

The stabilization of the thermodynamically stable α-phase in the dense chromia-doped alumina coatings was achieved using concepts based on the injection of hybrid feedstock (powder + suspension) and intermixed liquids (suspension + suspension; suspension + solution) in the plasma jet (Paper III) . "Foamy" full intermixing alumina-chromia coatings with reversible thermochromic behavior were prepared for the first time by SPPS (Paper IV). An improvement of the mechanical stability of these coatings is mandatory in order the coatings to be applied for real components.

The main objective is achieved.

Scientific value and overall evaluation

The thesis makes significant contribution to the development of ceramic oxide coatings prepared by new thermal spray processes. With WSP-H torch and liquid feedstocks new possibilities in the tailoring of the coating properties have been demonstrated. There are important achievements in this work, especially for the in-situ alloying and stabilization of the α-phase. Mechanical stability of solutions-intermixed coatings are still weak, but it is clear that this thesis represent only the initial step of a long-term development. For further work the evaluation of the electrical insulating and corrosion resistance properties of suspension / solutions coatings is highly recommended.

Mr. Tesař has demonstrated the ability to perform research and to deliver scientific results applicable in the field of material science and thermal spraying. I do recommend the thesis for presentation and defense with the aim of receiving the Degree of PhD.

Dresden, October 28, 2021

Filofteia-
Laura Toma

Digital unterschrieben
von Filofteia-Laura Toma
Datum: 2021.10.28
18:28:21 +02'00'

Dr. Filofteia-Laura Toma