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Opponent 's review on the habilitation thesis of Amirhossein Pakseresht, Ph.D entitled

"Plasma Sprayed Coatings: From Splat Morphology to Thermal Barrier Coatings".

Ceramic coatings prepared by plasma spraying technologies have found wide use in a number of applications, from engineering, aerospace, and rocket industry to electronic applications. From the point of view of chemical composition and microstructure, the coatings are based mainly on oxides of transition metals which form high-temperature phases with excellent physical, especially mechanical properties (high hardness, wear resistance, etc.). A few hundred micrometers thick coating of yttrium stabilized zirconia (YSZ) serves as an effective thermal barrier against high temperature oxidation and corrosion and protects the blades of aircraft engines and gas turbines, significantly increasing their efficiency and extending their lifetime. $BaTiO_3$ coatings have found their application in the semiconductor industry and sensors due to their dielectric and ferroelectric properties.

The physical properties of coatings and their behavior in given applications are determined primarily by technological preparation which leads to microstructural differences, high porosity, poor adhesion, etc. Secondly, it is the microstructural design of the coatings themselves, the combination of chemical elements, multilayer systems, functionally gradient coatings, etc. which leads to the improvement of physical properties.

In his habilitation thesis, Dr. Pakseresht presents his own scientific contribution to the issue of ceramic coatings in the form of 14 quality publications (12 CC) in which he is mostly mentioned as the first author. The set of works is preceded by a 25-page summary which indicates an introduction to the topic and summarizes the main results of articles in combination with published works by other authors.

I would like to summarize the most important results of Dr. Pakseresht which in my opinion shift the knowledge in the field of plasma sprayed coatings. Habilitant's scientific work focuses on the preparation of coatings using "Air Plasma Spray" technology, which is a fast, efficient, and relatively inexpensive method of plasma spraying but the starting powder requires suitable spheroidization. Dr. Pakseresht presented his own contribution to this issue in 4 articles where he replaced the traditional "slurry" processes of granulation by plasma processes and achieved a lower porosity of powders. This led to the application of low porous $BaTiO_3$ coatings with better physical properties compared to conventional equivalents. An equally important fact for the quality of coatings proved to be the heating of substrates where Dr. Pakseresht achieved a disk-like morphology of $BaTiO_3$ particles (splats) thereby compacting the microstructure and achieving better adhesion at the coating-substrate interface.

The development of thermal barrier coatings (TBC) is a key part of habilitant's research. In his work, he focuses on the basic pair: YSZ coating (top coat) + NiCrAlY (bond coat) which he modifies in various ways.

(a) Suppressed undesired martensitic transformations of ZrO_2 leading to high internal stresses and coating cracking. Here, Dr. Pakseresht introduced Sc and Ce as new dopants to stabilize the tetragonal structure. This increased the thermal stability of the SYSZ and improved the fracture toughness.

(b) Improved adhesion between the substrate and between NiCrAlY and YSZ coatings by forming functionally gradient bonding multilayers. In this case, Dr. Pakseresht achieved an almost defect-free microstructure and better mechanical properties.

(c) Improved resistance to thermal shocks. Dr. Pakseresht added a surface Al_2O_3 top coating formed by spraying a spheroidized nanopowder and created an effective barrier against oxygen diffusion. In this way, it slowed down the growth rate of the TGO layer at the coating-substrate interface and reduced stresses.

(d) improved the high-temperature corrosion resistance of the coatings against molten sodium and vanadium salts, where he also used the effect of the dopant Sc to stabilize the SYSZ structure. The coatings showed high corrosion resistance at 1050°C.

In other works, Dr. Pakseresht showed an original approach to the protection of casting steel with a high Si content against electrochemical corrosion by means of plasma spraying mullite – NiCrAlY. He published a new method for the preparation of YSZ coatings using SPS-based sintering techniques where he achieved a low-porous microstructure and a significantly lower proportion of transformed m-ZrO_2 after high-temperature exposure compared to coatings prepared by APS technology. He was the first to publish a new approach to improving the toughness of YSZ coatings by forming a composite with whiskers. In two publications, Dr. Pakseresht also presents approaches to controlling deposition parameters using neural networks to achieve the best combination of deposition parameters vs coating quality.

I also have several reservations about the formal side of the habilitation thesis. In the introductory part, for a better understanding of the topic, I miss the description and scheme of the used APS technology with a brief introduction of deposition parameters and their effects on the preparation of coatings. I am also hindered by the complete absence of accompanying and illustrative images to the written text, especially visual comparisons with publications of other authors. I admit that I read the attached articles first, and later the introductory text to better understand it. In conclusion, I would also welcome a briefly written vision of the direction of research in the field of APS and TBC. However, these comments do not diminish the scientific level of Dr. Pakseresht. It is indisputable and testifies to its high scientific level. This is also evidenced by the excellent scientometric parameters of the habilitant H-index = 15 and the number of citations of almost 900

according to the Scopus database. Also Dr. Pakseresht's participation in international conferences, invited lectures and, finally, pedagogical activities.

I also have a few questions for the work that should be answered during the defense:

1. In your work, you mention preheating of the substrate to 600°C, leading to the formation of disk-like particles, as one of the ways to reduce the porosity of coatings. Do you think that it would also be possible to reduce the porosity of the coatings by adding metal or alloy powders (to feedstock) that form a liquid or viscous phase during preheating or by post-deposition annealing to fill cavities and pores? Would that make sense? Are there any limiting factors?

2. The interface between the substrate and the bonding coating plays a crucial role in the adhesion and thus the life of the whole system. In your work, you state, without further consideration, as a standard procedure grit blasting and roughening of the substrate surface which should lead to improved adhesion. Would you be able to explain this fact in more detail? Have you ever performed a detailed microscopic analysis of the treated surface? Do the exposed ceramic phases (carbide grains) from the substrate play a role there? Is it possible to talk about physisorption or chemisorption of incident particles (splats) on the surface? Would chemical etching of the substrate surface be useful?

3. Fracture toughness significantly determines the behavior of TB during high-temperature exposure, with or without mechanical load. In your work, you evaluate fracture toughness rather by visual vision using SEM. Is it possible to perform a direct measurement of the stress intensity factor (K_{IC}) on plasma sprayed coatings or to determine in another micromechanical way some numerical value which evaluates the fracture toughness?

4. What do you think about plasma sprayed coatings based on transition metal diborides? Are they suitable, possibly in combination with other materials, for use as TBC?

5. Do you have experience with applying TBC to very promising γ-TiAl superalloys?

After evaluating the scientific outputs and pedagogical activities of Dr. Pakseresht, I clearly recommend accepting his habilitation thesis as a basis for the habilitation procedure at the Alexander Dubček University in Trenčín and after its successful defense to award him scientific-pedagogical title of **"docent"** in the field of Inorganic Technology and Materials.

In Bratislava 8 August. 2021

Doc. Ing. Marián Mikula, PhD