UNIVERSITY OF CHEMISTRY AND TECHNOLOGY, PRAGUE
Faculty of Chemical Technology
Department of Glass and Ceramics

Reviewer's report on the Ph.D. thesis (doctoral thesis) "Advanced Plasma-Sprayed Ceramic Coating Prepared from Liquid Feedstocks" by Ing. Tomás Tesař

Reviewer: Prof. Dr. Willi Pabst (UCT Prague)

The thesis deals with suspension and precursor solution plasma spraying (PS), which is are innovative coating methods, in contrast to the conventional PS of dry coarse powders, which is well established and industrially applied on a large scale. In Section 1 (14 pages) the candidate presents an overview on the state of the art in liquid feedstock PS, including the general background (PS equipment, feedstock injection, dry powder versus liquid feedstock, mixing of feedstock materials), in Section 2 (4 pages) an analysis of the deposition process (interaction between plasma jet and liquid, impingement on the substrate) is given, and in Section 3 (3 pages) alumina as a material for PS (properties and application) is presented, including a brief section on chromia-stabilized alumina. After a brief formulation of the objectives (1 page) the candidate explains in Section 4 the sample preparation and characterization methods (7 pages), including suspension preparation and feeding, spraying, microstructure analysis (mainly SEM with image analysis), chemical analysis (XRF) and phase analysis (XRD, NMR) and mechanical property testing (hardness, wear resistence, tensile adhesion strength), but for details the reader is referred to the "Collection of papers" in Section 5 (59 pages, including the 4 core papers), i.e. original full-length research articles published in impacted journals that constitute the main part of the thesis. This section is introduced by an overall flowchart, and each of the four individual papers is introduced by a small subsection commenting the content and summarizing the main results. This section ends with an overview of papers not directly to the core part of the thesis, but nevertheless closely related to the processes treated in the thesis. Section 6 presents a synthesis of results and Section 7 briefly summarizes the main conclusions and gives an outlook to future research. The work itself has 78 references, which is not very much for a PhD thesis, but these references have been judiciously selected and have a direct relation to the text. The Appendix lists, beside the 4 core papers of this thesis, in which the candidate is the first author, also 10 other impacted journal papers, in which the candidate is a co-author. A check on the Web of Science confirms that the candidate is the author or co-author of 14 impacted journal papers and has currently an H-index of 5, which is a very nice rating at this stage of the career.

I have no principal objections to any part of the work. The overall impression is excellent, and this impression is fully confirmed after a careful detail study of the work. So, all I can do in this case is to give a few minor comments and ask a few questions that might of more general interest. The candidate may answer them during the defense.

Comments and minor questions:

1. p. 13/14 and paper I, p. 278: What is the meaning of the abbreviation or unit "slpm"? It seems to me that it is not defined in the work.
2. p. 17: Momentum is defined as the product of mass and velocity, so it would seem logical to me to call the product of (mass) density and velocity a "momentum density", i.e. momentum per unit volume. So why is the velocity squared in this definition here?

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3. p. 21: What is the reason why on Figure 7 it is assumed that the suspensions do not form shells like in the case of precursor solution, if even the much larger ceramic suspension droplets in a conventional spray drier often do form hollow spheres (microballoons)?
4. p. 24: The term "strong alkali" is strange. Should be "strong alkaline solutions". Also the temperature, above which the α-phase of alumina occurs (i.e., 1100 °C or slightly higher, 1150 °C) is usually not called recrystallization temperature, but simply "transition temperature". Grain growth, to which the term "recrystallization" is sometimes referred, is not necessarily involved in this transition. Moreover, in the text the candidate says that α-Al_2O_3 is "rhombohedral", but in Table 2 he calls it "trigonal". The two terms are of course synonymous. However, the classification of α-Al_2O_3 (corundum) as "hexagonal", mentioned in a footnote to Table 2, is an old-fashioned Anglo-saxon or rather American tradition that has its roots in the fact that trigonal crystals can be described using the hexagonal coordinate system, but for α-Al_2O_3 (corundum) it is definitely wrong and should be avoided, because α-Al_2O_3 (corundum) has 6 independent elastic constants (as for trigonal crystals) and not 5 (as for hexagonal crystals).
5. p. 24: The candidate claims – albeit with some reservation, "possibly" – that "the easiest way to obtain a coating comprising the α-phase is maintaining high substrate temperature … in order to decrease the cooling rate of the splats". However, if the desired cooling rate, mentioned in the text on p. 24, is in the range 1–100 K/s, and the cooling rate of the splats is of order 10^8 K/s (as mentioned on p. 17 and p. 22) or 10^6 K/s (as mentioned in one of the papers), how could an increase of the substrate temperature have any significant effect on the cooling rate of the splats? If yes, should the substrate have in this case a temperature higher than 1100–1150 °C or can it have a lower temperature?
6. In paper I, p. 277 the authors use the abbreviation SPS for "suspension plasma spraying". Apart from the fact that – in the context of the candidate's work – the same abbreviation could stand for "solution plasma spraying", it is a well-established abbreviation for "spark plasma sintering" (which is, as the candidate certainly knows, the most frequently used term for the most popular popular electric current assisted sintering (ECAS) technique, although this technique has nothing to do with a plasma). Therefore, introducing this abbreviation here, while hardly using it in the papers, is not very wise. Also in my opinion "precursor solution plasma spraying" (PSPS) would be a more adequate term and abbreviation than "solution precursor plasma spraying" (SPPS).

Questions of more general interest:

1. p. 24 (and papers III and IV): The candidate mentions an "amorphous alumina" phase in addition to the two "transition aluminas" (γ and δ). Are there any properties (mechanical or thermal) known in the literature for this amorphous phase?
2. p. 25 (and paper IV): I understand that chromia is a clever way to stabilize the α-phase of alumina. However, working with chromium compounds always evokes the question, whether there are potential health hazards, either from the viewpoint of hygiene at the workplace or from the viewpoint of later application, including ecological hazards. Therefore, for example, in the refractory industry the use of chromium compounds is restricted to the absolute minimum (i.e. indispensible products for very special

applications). In powder processing this question might be even more urgent (danger of inhalation etc.) I would be interested in the candidate's opinion, whether somewhere in the process or during application, e.g. due to erosion or corrosion of the plasma-sprayed layers, such hazards can occur. In particular, under what conditions could hexavalent (as opposed to trivalent) chromium become an issue?

3. p. 32: The image analysis procedure shown schematically in Figure 16 would need a slightly more detailed explanation. First of all, it should be mentioned that the volume fraction of pores and cracks has been estimated here via the area fraction of pore or crack sections, assuming the validity of the Delesse-Rosiwal law. (This of course just my guess, since it is not explicitly stated in the work.) Strictly speaking, the Delesse-Rosiwal law is not necessarily valid for anisotropic microstructures. Did the candidate take this into account and use some corrections? Secondly, if the "fine porosity" has been determined in the regions that have been counted as apparently non-porous under low magnification, the total porosity is not exactly the sum of of coarse and fine porosity, but the amount fine porosity has to be multiplied by the percentage of apparently non-porous regions before adding it to the "coarse porosity". Has this been taken into account? Thirdly, how did the automatic image analysis routine exclude in the measurement of the "fine porosity" the part of the porosity that has already been counted as "coarse porosity" and vice versa? Points two and three, if not considered, would have lead to an overestimation of the total porosity. Of course all this concerns only the absolute values. For the purpose of relative comparison any consistently applied procedure would be adequate.
4. In paper I, p. 282 it is shown that the commercial suspension (Treibacher) has very good rheological behavior (shear thinning flow curves) at signifcantly higher solids loading than the IPP suspensions. This is attributed by the authors to the larger grain size, which is indeed a possible reason, but should also be visible in a significantly reduced sedimentation stability. Unfortunately, these sedimentation stability results are not reported for the commercial suspension. Have they been measured? Another reason can be be addition of a dispersant / deflocculant. In particular, for smaller particles it may be very important to disperse the particles by ultrasonics (to deagglomerate the suspensions) and an appropriate dispersant / deflocculant (to prevent re-agglomeration). Has this been done with the IPP suspensions?
5. In paper III, p. 303 the increasing branch of the viscosity curve for suspension S-A shows a viscosity much lower than 1 mPas, increasing with increasing shear rate, which is of course a measurement error. Much more disputable, however, is the fact that the viscosity of the alumina and alumina-chromia suspensions with 20-30 wt.% is more than 2 orders of magnitude (!) lower than of the 25 wt.% chromia suspensions, although the volume fractions are at least comparable (it has to be noted that chromia has a higher density than alumina!). How does the candidate explain this?
6. It is a nice idea to supplement XRD phase analysis by NMR (papers I and III). In paper III, p. 307 the comparison between XRD and NMR shows satisfactory agreement. Does NMR provide wt.% or vol.%? Is there a fundamental paper that proves that NMR provides wt.% that can be directly compared to XRD?

The thesis treats a timely topic, and is without doubt a valuable contribution to current research and development in the field of PS processing. There are several features the

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combination of which makes this thesis unique: First the use of the hybrid water/argon-stabilized plasma torch, second the general idea to compare powder, liquid and hybrid feedstocks, third the wide scope of the work ranging from feedstock rheology to phase analysis (by both XRD and NMR) microstructure analysis (by SEM-based image analysis) and property testing (hardness, wear, adhesion) and, last but not least, the realization of chromia doping to increase the α-phase alumina content after deposition and the reported thermochromic behavior. The combination of these features makes this thesis an internationally competitive research work.

The methodological approach, albeit completely empirical, is sound and reasonable. I appreciate the plausible combined treatment of feedstock characterization, processing issues, microstructure characterization and property testing. In all these fields the candidate showed remarkable insight, which proves that he has deeply studied, thoroughly understood and judiciously applied the relevant methods, including a considerable amount of innovative ideas.

All objectives of the work can be considered as fulfilled without any reservation. Concerning the results, I have absolutely no objections. Both the text of the thesis itself and the four core papers are well written in a clear and logical style with a plausible interpretation of results. It is highly probable that the four papers have undergone careful review, because as a reviewer I also would accept them as they are now. Thus this thesis is a fully-fledged high-level research work, as evidenced also by the citations from the PS community. The high scientific value of the work consists in the fact it provides cutting-edge solutions for ceramic coating technology with a high applicational potential. The concept of suspension and precursor solution PS is a generic one that can be applied to many other ceramics systems, as shown for example in the impacted journal papers, in which the candidate has been a co-author.

The English of the thesis and the impacted journal papers is excellent, both grammatically and stylistically, with extremely few mistakes (negligibly few) and, as far as I can see, no misprints. From the formal point of view the thesis seems perfect to me. Moreover, formally and stylistically this thesis makes an interesting overall impression that indicates at the same time scientific enthusiasm and intellectual maturity exceeding the level commonly expected for Ph.D. candidates from engineering fields.

With respect to the aforementioned facts **I recommend this Ph.D. thesis for defense** without any reservation and to award the title “Ph.D.“

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