Surface & Coatings Technology 325 (2017) 277–288

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

# Development of suspension plasma sprayed alumina coatings with high enthalpy plasma torch

Tomas Tesar [a,*], Radek Musalek [a], Jan Medricky [a], Jiri Kotlan [a], Frantisek Lukac [a], Zdenek Pala [a], Pavel Ctibor [a], Tomas Chraska [a], Sarka Houdkova [b], Vaclav Rimal [c], Nicholas Curry [d]

[a] Institute of Plasma Physics CAS, v.v.i., Department of Materials Engineering, Za Slovankou 3, 182 00 Praha 8, Czech Republic
[b] New Technologies Research Centre, University of West Bohemia, Univerzitni 8, 306 14 Plzen, Czech Republic
[c] Charles University, Faculty of Mathematics and Physics, V Holesovickach 2, 180 00 Praha 8, Czech Republic
[d] Treibacher Industrie AG, Auer-von-Welsbach-Straße 1, 9330 Althofen, Austria

A R T I C L E   I N F O

*Article history:*
Received 15 March 2017
Revised 14 June 2017
Accepted in revised form 15 June 2017
Available online 16 June 2017

*Keywords:*
Suspension plasma spraying
Aluminium oxide
Mechanical properties
Hardness
Adhesion
Wear resistance

A B S T R A C T

Deposition of aluminium oxide ($Al_2O_3$) coatings from liquid feedstocks using a high enthalpy hybrid water-stabilized plasma torch was investigated. The entire process included the optimization of spraying parameters using a commercial ready-to-spray suspension, optimization and deposition of custom-made suspensions and one solution and evaluation of mechanical properties of the most durable coatings. Acquired coating microstructures varied from porous with typical columnar morphology to well-sintered dense structures with low porosity. The microstructural features were clearly linked to the feedstock formulation. The most durable coating with the highest density microstructure prepared from ethanol-based suspension showed outstanding mechanical properties, e.g. high values of hardness (up to 1211 HV0.3), tensile adhesion strength (up to 51 MPa) and wear resistance (material removal rate as low as $1.94\cdot10^{-5}$ $mm^3\cdot N^{-1}\cdot m^{-1}$ as measured by pin-on-disc test). Moreover, deposition from a water-based solution of aluminium nitrate resulted in deposition of highly porous coating composed predominantly of stable α-alumina phase.



## 1. Introduction

Aluminium oxide ($Al_2O_3$) coatings are commonly used in various applications where good chemical and thermal stability, electric insulation or wear resistance are required [1]. These coatings are usually prepared by atmospheric plasma spraying (APS) technique using coarse powders of typical particle size in tens of micrometers. However, suspension plasma spraying (SPS) has lately gained immense attention since it provides the possibility to prepare finely structured (even nanostructured) coatings with better functional properties than with conventional coating techniques. The main benefit stems from the fact that very fine powders, typically with particle size in tens or hundreds of nanometers, are introduced into the plasma jet in the form of a suspension. After the carrier liquid (solvent) is evaporated, the small melted particles form a coating with structural units in the submicron range [2]. Another added value for alumina spraying is the possible retention of the initial α-phase of the powder and preparation of the desirable α-phase rich coatings [3]. This stable phase is favored for its high hardness and corrosion resistance. Conventional plasma spraying of powders generally leads to coatings with high content of metastable γ and δ phases due to the rapid cooling of the deposited material [4].

The resulting coating microstructure is, however, a function of many variables, such as plasma characteristics (enthalpy, density, velocity, etc.), feedstock properties, and process parameters (standoff distance, feeding distance, feed rate, etc.) to name a few [5]. It may be challenging to find the right set of parameters for a specific application but it also provides desirable potential of variability of the deposition process for the fine tuning of the coating microstructure through modification of the input parameters. The relations between the operating parameters and the coating properties need to be understood to be able to tailor the microstructure for a desired application.

One of the key parameters governing the coating build-up are the properties of selected feedstock, i.e. in the case of SPS it is the suspension concentration (solid load), solvent type, additives, etc. which influence fragmentation of the feedstock in the plasma jet. According to results obtained for gas-stabilized plasma torches [6–8], it is generally assumed that water-based suspensions lead to more compact microstructures whereas alcohol-based ones lead to less dense, porous microstructures. This is usually attributed to the fact that water forms bigger droplets due to the higher surface tension and the resulting particles impinge the surface more perpendicularly and with higher momentum than the smaller ones. However, the bigger droplets with lower degree of atomization

* Corresponding author.
*E-mail address:* tesar@ipp.cas.cz (T. Tesar).

http://dx.doi.org/10.1016/j.surfcoat.2017.06.039
0257-8972/

may result in the presence of unmelted material embedded in the coating due to insufficient melting of the core of particle or agglomerates [6, 9]. If presence of this feature (i.e. untreated feedstock) is not desirable, it may be mitigated by modification of the suspension atomization to yield smaller droplets (e.g. by lowering the liquid surface tension or by pre-atomization of the feedstock before injection into the plasma jet [10]), by choice of the injection point position or torch standoff distance from the workpiece to ensure optimal melting of the powder.

An alternative route of plasma spraying with liquid feedstocks is solution precursor plasma spraying (SPPS), where the deposited material is prepared in-situ from the solution injected into the plasma jet [11–13]. A major benefit of this approach is that the feedstock does not contain any solid particles, which for example eliminates the risk of sedimentation and, in case of a solution of multiple chemicals, the homogenization is significantly facilitated. On the other hand, both SPS and SPPS share the same challenges as compared to the conventional spraying of powders in terms of additional energy consumption due to the solvent evaporation or the relatively low deposition rate achievable as compared to conventional spraying.

The use of a liquid carrier in SPS and SPPS raises the need for high enthalpy plasma source, as substantial amount of heat is required for the processing of the feedstock, i.e. heating and evaporating of the liquid followed by heating and melting of the powder. From this point of view, torches based on water stabilization of plasma (WSP technology) provide a high enthalpy plasma jet, which makes them particularly suitable for preparation of coatings from liquid feedstocks [14,15]. The most recent “hybrid” WSP technology (WSP-H) combines the principles of gas (GSP) and water vortex (WSP) arc stabilization producing plasma jet of relatively low density (about 6.8 $g \cdot m^{-3}$) but high enthalpy (up to 300 $MJ \cdot kg^{-1}$) and high velocity (up to 7000 $m \cdot s^{-1}$) [16,17]. Due to these plasma characteristics, WSP-H torch was proven to be convenient for large-scale coating production due to a high achievable feedstock throughput (more than 100 ml of suspension per minute) combined with high deposition efficiency [15,18].

This paper examines the possibility of suspension plasma spraying of aluminium oxide with WSP-H plasma torch at high feed rate. The entire process is described, including the optimization of suspensions, the deposition of coatings, and the evaluation of mechanical properties of the deposits. The aim of the study was to find suspension formulations suitable for WSP-H spraying, to prepare durable dense coating microstructure with low porosity and possibly high α-phase content, and to compare the coating properties with those of conventional powder-sprayed coating deposited also with WSP-H. Possibility of using WSP-H torch for solution plasma spraying of alumina will also be illustrated on the deposition of coating with extreme porosity (up to 70%).

## 2. Experimental

Firstly, optimization of the deposition parameters was carried out using a commercial ready-to-spray water-based suspension. Three feeding (injection) distances were tested (19, 25, and 31 mm) in order to evaluate how much this parameter influences the resulting coating microstructure for WSP-H technology. Next, optimization of custom-made suspensions (further denoted as IPP suspensions) was carried out in order to attempt deposition from suspensions of different formulation to possibly obtain various microstructures. Attention was paid to the optimization of suspension formulation in terms of sedimentation stability and viscosity. Two commercially available powders with different particle size distributions were used to formulate both water and ethanol-based suspensions. In the next step, the optimized IPP suspensions were also used for the deposition of coatings. At last, water-based solution of aluminium nitrate nonahydrate was sprayed to test the feasibility of solution precursor plasma spraying of alumina with WSP-H technology.

Microstructure and phase composition of all suspension and solution-sprayed deposits were evaluated. In the last step, mechanical properties including hardness, adhesion/cohesion strength and wear resistance in dry and wet conditions were measured for one selected coating from the commercial suspension and one from the custom-made suspension. Coatings were compared with the coating deposited by WSP-H torch using conventional plasma spraying of coarse dry powder.

### 2.1. Feedstocks

Commercial ready-to-spray water-based suspension of α-alumina powder ($d_{50} = 2.2$ μm) with 40 wt% solid particle content supplied by Treibacher Industrie AG (Austria) was used for the optimization of the spraying parameters. To formulate the custom-made IPP suspensions, commercial α-alumina submicron-sized powders with nominal particle sizes of 300 and 1000 nm (as designated by manufacturer - Allied High Tech Products, INC, USA) were dispersed with 10 and 20 wt% solid concentrations in water or ethanol solvents. Micrographs of both powders are compared in Fig. 1 revealing partial agglomeration and noticeably bigger particles of the 1000 nm powder. For preparation of the solution, aluminium nitrate nonahydrate $Al(NO_3)_3 \cdot 9H_2O$ (Lach-Ner, s.r.o., Czech Republic) was dissolved in water with the concentration of 5 wt% of aluminium in the solution. For the deposition of the conventional coating, SURPREX AW24 powder was used (Fujimi INC., Japan, granulometry $-75 + 38$ μm).

For the stabilization of the IPP suspensions, BYK-LP C 22587 stabilizer (BYK-GARDNER GmbH, Germany) was used in concentration of 0.5 wt%. Sedimentation resistance of the prepared suspensions with 20 wt% of solid phase was compared to that of the non-stabilized ones. Sedimentation process was monitored using an automated time-lapse camera taking photographs of the suspensions in test tubes regularly over a time period of 4 h. The sedimentation progress was evaluated as the position from the distinguishable sediment-solvent interface to the initial liquid column height.

Viscosity of suspensions selected after the sedimentation evaluation was measured using DV2TLV viscometer (Brookfield, USA) with coaxial cylinder-cylinder geometry. An automated regime was used measuring a sequence of speeds from 10 to 100 and back to 10 RPM with 10 RPM increment (decrement) taking 5 measurements averaged over 2 s at each speed.

### 2.2. Deposition process and design of experiment

The design of deposition experiments (see Table 1) is reflected also in the experiment code in the form of *XXsolventYY* which comprises of the feeding distance in mm (*XX*), solvent used (“W” for water-based IPP suspensions, “E” for ethanol-based IPP suspension, “Tr” for the commercial water-based Treibacher suspension, and “Sol” for the water-based IPP solution) and solid phase concentration in wt% (*YY*). All other parameters of the deposition were constant for all experiments. The custom made suspensions were prepared by adding the 300 nm nominal particle size powder (see Fig. 1a) and stabilizing agent to the solvent while maintaining continuous mechanical stirring. The mixture was then subjected to one hour long mechanical stirring in a cylindrical mill with a set of ceramic balls to further homogenize the feedstock and disintegrate agglomerates. The solution was prepared by mixing the required amount of $Al(NO_3)_3 \cdot 9H_2O$ (5 wt% of Al in the solution) until completely dissolved.

Conventional coating for benchmarking of mechanical properties was prepared from alumina powder according to the deposition process parameters listed in Table 2. The rather long spraying distance of 380 mm was chosen based on the long term experience with spraying of alumina powders using WSP-H torch as the selected conditions provide a reasonable compromise between the coating porosity and deposition efficiency.

Hybrid water-stabilized torch WSP®-H 500 (ProjectSoft HK a.s., Czech Republic) operated at 500 A (~150 kW) was used for deposition with argon flow of 15 slpm [17]. For all deposition experiments, radial