The effectiveness of prevailing plasma spray conditions in the synthesis of protective coatings

Vitas Valinčius, Viktorija Grigaitienė, Pranas Valatkevičius, Liutauras Marcinauskas
Lithuanian Energy Institute, Plasma Processing Laboratory, Kaunas, Lithuania
vitas@mail.lei.lt

Introduction. Protective and catalytic coatings of different composition are widely used in diverse fields of industry including a modification of surface layers of constructional materials. Mechanisms of film formation in plasma spray processes are not investigated thoroughly. It is not determined how the parameters of process influence the quality, specific surface area, thickness and adhesion of coatings [1,2]. Therefore the investigation of the influence of formation technology on structure and properties of protective ceramic coatings is the main objective of present work.

Experimental equipment. Coatings in the present study were deposited employing a specific plasma spray technique with a linear, sectional plasma generator (PG) 50-70 kW of power generating non-equilibrium plasma jet at atmospheric pressure. Plasma stream reactor was connected to the plasma torch exhaust nozzle.

The main parts of the equipment are: plasma torch with electricity supply, gas supply, cooling, operation control and data monitoring systems. Power supply system consists of direct current (DC) power source capacity up to 1 MW with smooth current tuning, rheostat and arc excitation facility. The gas supply system contains pressure vessels containing compressed gas, air compressor, pipelines and high accuracy mass-flow controllers. Clean dry air was used as plasma forming gas. The mass flow rate of gas was controlled by valves and monitored by diaphragms and critical nozzles.

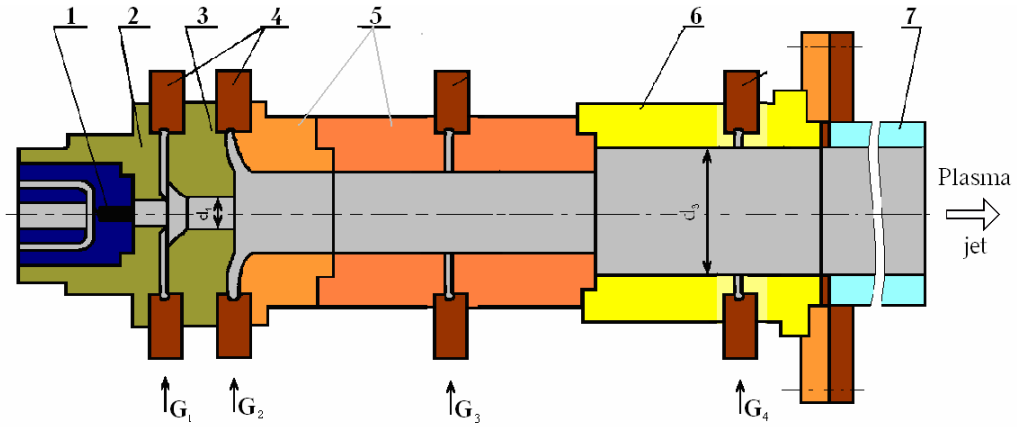


Fig.1. The schematic presentation of a linear sectional DC plasma torch. 1 – cathode with hafnium emitter; 2 – cathode junction; 3 – arc ignition ring, 4 – insulating rings with holes for feeding of plasma forming gas G_1, G_2, G_3 and G_4; 5,6 – step-formed anode; 7 – circular exhaust nozzle

The PG arc current varied in the range of 150–200 A. The voltage drop depended on the gas flow rate and ranged from 300 to 450 V. The operating gas was injected at the cathode (G_1) and anode (G_2) side. The substance in the form of dispersed particles less than 50 micrometers in diameter were injected via tangential holes made in insulating rings (G_3 and G_4) together with a small amount of carrying gas (air). The total air flow rate through the PG was $G = G_1+G_2+G_3+G_4 = (5–8)\cdot10^{-3}$ kg·s^{-1}. Experiments were performed at the mean plasma flow temperature 3000–4000 K and the mean velocity 500–550 m·s^{-1}.

During the experiments on the effect of PG operating regime, coatings were deposited with intermediate layers of Al powder on stainless steel substratum supplying outside the reactor into exhaust plasma jet at the distance x/d=0.5 from the exhaust nozzle. Aluminum hydroxide particles up to 50 μm of diameter were mixed with copper oxide particles up to 50 μm using mass ratio 10:1. 75% of initial powder was injected via blowholes into the reactor and 25% outside the reactor. Experiments were conducted at three regimes of PG changing arc current from 180 A at the constant flow

rate of plasma forming gas (Table 1). The power supply of this plasma torch was P = 50–70 kW. A similar plasma source is described in detail elsewhere [3]. Depending on plasma process regime (arc current and voltage), films of 30 – 70 micrometers in thickness were formed from $Al(OH)_3$, TiO_2 and CuO containing powder mixtures on the metal strips. The similar coatings were deposited using other ceramic based powder containing dolomite and quartz sand mixture. Depending on demand, practically any metal oxides such as iron, cobalt, nickel, etc. were added to the mixture. The structure of coatings was evaluated from the top-view and cross-sectional scanning electron microscopy (SEM) observation and the surface phase composition was analyzed by X-ray diffractometer.

Table 1. Plasma spraying regimes for ceramic coatings deposition

Spray regime	1	2	3
Arc current, A	180	190	200
Arc voltage, V	320	325	322
Power, kW	57.5	61.7	64.5
Total gas flow rate, 10^{-3} kg·s^{-1}	5.03	5	5.03
Exhaust mean velocity, m·s^{-1}	510	530	550
Exhaust mean temperature, K	3560	3650	3820
Spray distance, mm	120	120	120

Results and discussion. It was determined, that during plasma spray process the powder was partially melted and spheroidized whereas the initial ceramic based dolomite and sand mixture powder were in the form of agglomerates. It has been found, that the shape and size of the grains on the coating depend on characteristics of the plasma source and gas flow rate. Under high plasma forming gas flow rate and low temperature in plasma chemical reactor, the feeding dispersed particles does not melt fully in the same time and may be carried out as partly melted and agglomerated granules [4]. The small amount of hydrogen improved the deposition efficiency and increased the energy transfer.

The dependence of spraying parameters on the structural changes of aluminum hydroxide coatings was studied from SEM micrographs and is shown in Fig. 2. The microstructure of coatings contains certain amount of pores and voids. However, it is seen, that proper choose of deposition regime has a direct influence on the coating quality. The structure of the coating deposited at lower temperature (regime 1) is characterized by porous nature (Fig. 2, b). The distribution of pores is quite homogeneous. Reduced porosity is specific to the coatings deposited at higher temperature, but these coatings are qualified by finer structure and increased density (Fig. 2, c). X-ray diffraction analysis of plasma-sprayed $Al(OH)_3$, quartz sand and dolomite mixture shows the domination of amorphous substances with a small amount of crystalline phases of mullite, corundum, quartz, cristobalite in all the products obtained. The presence of amorphous or crystalline phase or other properties of the product may be regulated also by means of variation of mean plasma parameters.

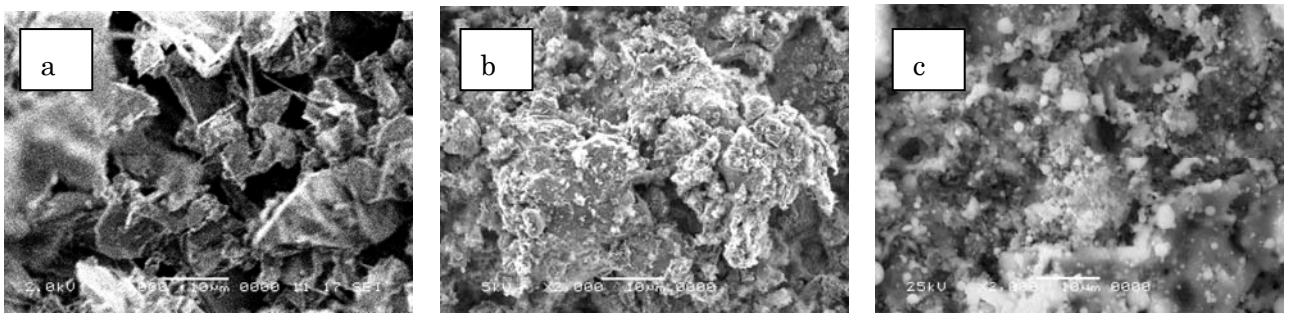


Fig. 2. SEM image of coatings produced of $Al(OH)_3$ and 10% CuO mixture at different plasma source regimes showed in Table 1: a – initial powder; b – regime No1; c – regime No3

By XRD patterns the dominated phase of the initial powder is rutile and the second phase is anatase (Fig. 3, 1). In the XRD patterns of plasma-sprayed titanium there is no new phase. It was observed that the peak intensities present some difference according the plasma process regime. As the process temperature was increased (Table 1, regime 3), the intensity of the main peaks is increased indicating an increased degree of crystallographic texture in the plasma deposited titanium. X-ray analysis of $Al(OH)_3$ coatings doped with metal oxides shows the presence of α-Al_2O_3 and γ-Al_2O_3 phases. It is shown that the ratio of phase fraction depends on the substrate temperature. Pure α-Al_2O_3 is obtained if the substrate temperature exceeds 760 ^oC.

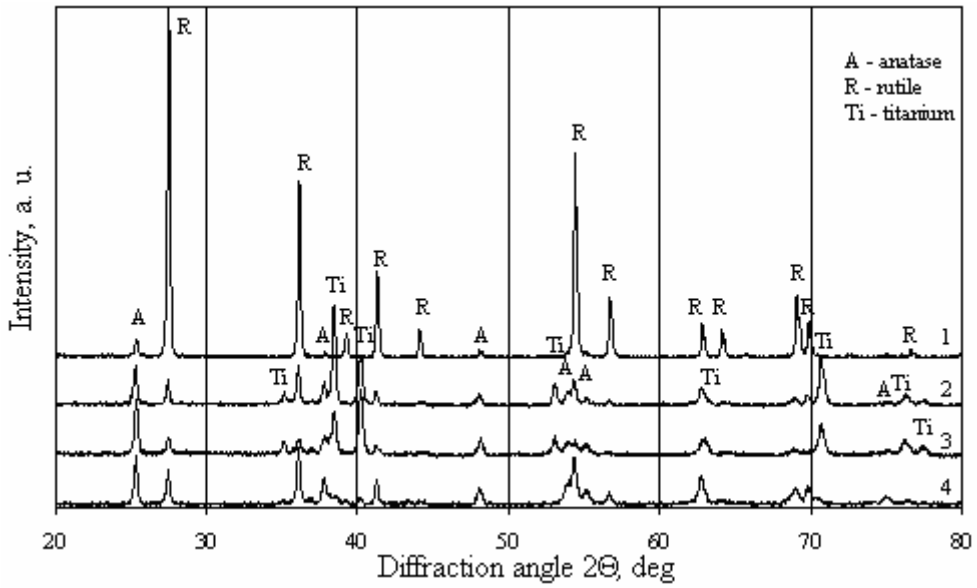


Fig. 3. The XRD patterns of titanium at different plasma source regimes in table 1: 1 – initial powder; 2 – regime No 2; 3 – regime No 1; 4 – regime No 3

With the increasing temperature, the pore size decreases. This means that increasing arc current in the plasma source, the particles on the coating became more porous because of plasma spray pyrolysis process [5] which may occur in certain conditions during the interaction of particles with the plasma jet. However, after the injection of small amount of hydrogen, the temperature may become as the most important parameter. Besides, for the reason of high temperature, the dispersed particles in the jet is fully melted and partly evaporated before they reach the substratum. Since deposited coatings have a good adhesion and mechanical strength, however their porosity and specific surface area is rather low (Fig. 4). Such coatings are suitable in tribological application, however is inapplicable in the catalysis.

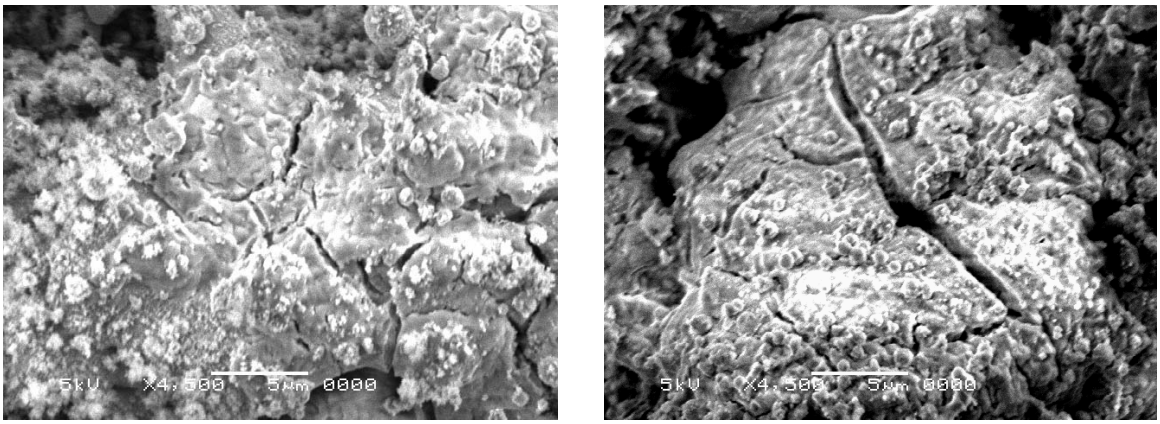


Fig. 4. SEM micrographs of plasma-sprayed aluminum hydroxide powder injected directly into reacting arc zone before arc spot: left – regime No 1, right – regime No 3

In all other cases, the surface structure of the coatings in the SEM observation shows that the coatings deposited using the plasma spraying are of good quality, thick, rough and homogeneous. Randomly distributed pores of different sizes are observed. The average coating thickness evaluated by cross-sectional SEM observation was from 35 μm to 50 μm and more. By the results, all plasma sprayed metal oxide coatings are well adhered to the substrate. The coating thickness depends mainly on the spray duration.

The plasmas generally can be produced by the application of a sufficient high level of energy, e.g., in the form of arcs, sparks, glow discharges, flames or shock waves. It is the activated state of medium where the individual types of particles, e.g. ions, electrons and neutral particles (in the form of non-excited and excited atoms, molecules and radicals), can be grouped in accordance with different temperatures. Thanks those properties, atmospheric pressure arc plasma in touch with material stands out series properties, which are not possible to receipt at using another method of deposition [6,7]. The most important property is high power density, which is supplied to the material, its income up to 1 $kW \cdot cm^{-2}$ for continuous radiation and – uniquely to 1 $kW \cdot cm^{-2}$ (and even more) for pulse radiation.

Since constructional materials working temperature is up to 800 ^{o}C, the plasma-sprayed coatings were heat treated at this temperature for 10 hours. Microscopic analysis showed no substantial changes when compared to the not heat-treated samples. Post-treated coatings are qualified by finer and reduced porosity and increased density due to grain growth and sintering.

Conclusions

The use of the non-equilibrium plasma spraying technology at atmospheric pressure demonstrates the ability to obtain coatings with controlled characteristics for special applications. The prevailing properties of the final product obtained in plasma may be modified by the plasma source operational parameters and plasma jet characteristics.

Ceramic coatings have excellent characteristics such as fine and narrow size distribution, pure phase and spherical morphology. By the results, all plasma sprayed coatings are thick, porous, homogeneous and well adhered to the substrate. No substantial changes in the coatings microstructure were observed after the thermal annealing. Properties of prepared coatings (thickness, density, etc.) depend mainly on the precursor‘s chemistry, plasma jet parameters and exposure time, the plasma torch construction and optimal parameters.

Acknowledgement

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