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Structural and Surface Analysis of Plasma Processed Zirconia Coatings

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This paper reviews plasma deposition method of zirconia based ceramic coatings with regard to tribological applications. Subjects discussed include wear-resistant coatings from yttria-stabilized zirconia (YSZ) processed by plasma-spray technique on the stainless steel substrates employing non-equilibrium plasma spray technology at atmospheric pressure. The relation between the microstructure, surface texture and microhardness of the as-sprayed coatings was investigated.
Keywords: coating, plasma spraying, microstructure, YSZ.

INTRODUCTION

Performance parameters of the materials may be enhanced through engineered interface and surface modification techniques, such as functional coatings for electronic, optical and magnetic applications, biomedical coatings, surface modification by plasma, ion, and laser beam techniques, corrosion and oxidation resistance coatings, ultra hard coatings, etc. [1 – 3].

Engineering coatings find large application in all up-to date branches of industry during the last decades. The increasing requirement for high technology materials with specific properties in various types of environments has dictated that these materials possess near-surface properties different from its bulk values [4 – 5]. It concerns also thin ceramics coatings, deposited on various surfaces. New developments in coatings and surface engineering increase the lifetime of critical components and materials. The appliance of each ceramic coating is very individual and depends on the mechanical, electrical, thermal and biochemical properties [2, 3, 6]. The required properties of ceramic materials can be optimised by the processing method and its parameters because of the strong dependence between processing, microstructure and properties [5].

High temperature oxide ceramics and coatings, based on zirconia oxide are widely used due to their superior properties [7 – 8]. These materials are characterized by high hardness and high abrasion resistance, good corrosion resistance and biocompatibility and therefore, hard and wear resistant ceramic coatings are often used to improve the surface properties of the materials. Ceramics can be used as coatings to improve the wear properties and the biocompatibility of metal implants [9 – 10]. Plasma sprayed biomedical coatings on Ti alloy substrates are widely used as implant materials in orthopaedics due to their tribological properties and mechanical strength [9].

Thermal spraying is an attractive coating technique as it offers a wide choice of materials and processes in the high-tech ceramic field [10 – 11]. Thermal-sprayed refractory coatings are used for the life extension of engineering components [3]. Plasma spraying is one of the most accessible deposition processes bringing the solution to industrial problems. The versatility of this technology enables easier deposition of nanostructured materials, characterized by ultra fine grain size with excellent mechanical properties and are widely used as wear resistant coatings: from engines to artificial hip joints [12].

Plasma spray parameters influence the coating microstructure and film adhesion [3].

The results reported in this study represent the structural data of plasma sprayed zirconia coatings deposited on stainless steel substrates employing non-equilibrium plasma spraying technology at atmospheric pressure [13], suitable for various engineering applications. To predict the wear properties of plasma sprayed ceramic coatings, in this study we report some results of microhardness measurements and surface roughness parameters for two groups of plasma sprayed coatings with different composition of yttrium stabilized zirconia – 5.2 wt% and 10 wt% – 15 wt%. The relationship between microstructure of plasma spayed coatings, plasma process parameters and properties of coatings have been studied.

EXPERIMENTAL

The low temperature plasma spraying equipment used in this experiment was developed at Lithuanian Energy Institute (Fig. 1). The experimental equipment consists of these main systems: electricity supplies (1 – 3), plasma torch with a stream reactor for powder injection (10), gas supply and monitoring system (11 – 14), cooling system (15, 16) and operation control and data monitoring system (4 – 9). Continual data monitoring of operating plasma torch allows the test bench functioning.

Experiments were performed by linear single-chamber plasma torch [14 – 15]. Such plasma torches have very stable operating parameters (outlet plasma jet temperature and velocity). Average outlet jet temperature and velocity was determined from heat balance. The capacity of plasma torch, mass flow of gases, cooling water and its temperature were measured and gas enthalpy calculated.

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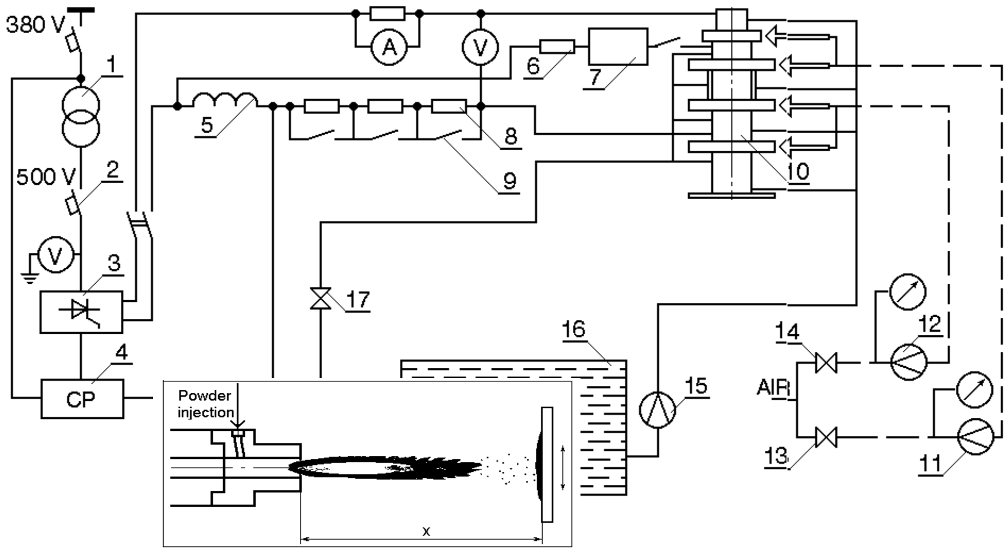


Fig. 1. Experimental set-up

A stream reactor for powder injection was constructed so that powders injection could be provided internally or externally. Internal powder injection was arranged at different positions, extending in this way spraying optimum conditions for different materials. The reactor appears as cylinder 150 mm in length and 7 mm in diameter made from stainless steel. At the distance of 100 mm from outlet nozzle there was arranged a place for hydrogen injection. Injection of hydrogen was used to vary outlet plasma jet temperature and velocity, while plasma torch parameter was stable [16]. Parameters of the plasma torch ranged within the following limits: power supply (*P*) – 35 kW – 40 kW, arc current (*I*) – 120 A – 200 A, voltage (*U*) – 225 V – 300 V, total gas flow rate (*G*) – 4.9 gs^{-1} (main gas flow rate throw plasma torch – 2.65 gs^{-1}, additional – 2.25 gs^{-1}, hydrogen – 0.12 gs^{-1}). Average plasma temperature in the powder injection place – 3300°C – 3700 °C, outlet plasma temperature – 2750°C – 3300 °C, average velocity – 650 ms^{-1} – 1350 ms^{-1}, the working gas – air.

A commercial yttria-stabilized zirconia powders with different amount of yttria (5.2 wt% and 10 wt% – 15 wt%) were used for plasma spray deposition. After being dried the powders were used to form plasma sprayed coating on the substrates. To obtain a uniform coating, the substrates were placed on the fixture, which could rotate during plasma spraying, 20 mm – 100 mm away from the exit of the torch. Prior to plasma spray, the substrate surface was hand-polished to 0.5 μm finishing.

All substrates were cleaned by acetone and dried in air before they were used. The substrates were placed at the distance of 70 mm from reactor exit and fixed on cooled plate. The plasma torch moving in horizontal direction may form the coating. Deposition time was 30 s. The thickness of the steel substrates was 1.2 mm.

Tests were carried out in order to compare the properties of sprayed samples versus plasma deposition parameters. We have focused the study on the following parameters: surface roughness and microhardness of as-sprayed coatings. For the cross section analysis the samples were mounted with epoxy resin and polished. The surface morphology of deposited layers was characterized using Scanning electron microscopy (SEM, JSM 5600) views. Vickers microhardness tests with a load of 50 g were performed on the polished surfaces of coatings by means of hardometer PMT-3 (Russia). The surface roughness of plasma sprayed zirconias was measured by means of surface analyzer – profilometer HOMMEL TESTER T500 (Germany). The phase composition of the started powder as well as sprayed films was analyzed by X-ray diffractometer (XRD, DRON-6) with Cu-K_{α} radiation. The mean crystallites size was estimated from integral breadths of the diffraction profiles by XFIT program [17]. The density and porosity of plasma-sprayed films were evaluated from the data of SEM analysis. The film thickness was evaluated from the cross-sectional scanning electron microscopy observation.

RESULTS AND DISCUSSION

Two groups of zirconia coatings were plasma processed on steel substrates using yttria stabilized zirconia powders (Cerac, USA). Table 1 presents the characteristics of the started powders investigated in the present study.

Table 1. Properties of YSZ powders for plasma spraying

Powder type	Yttria content, wt%	Particle size, μm	Purity, %
YSZ-1	5.2	63-100	99
YSZ-2	10-15	44	99

The main process parameters are presented in Table 2. The coatings were deposited at analogous spraying temperatures. The other deposition parameters – spraying distance and duration were kept constant.

Effect of spraying parameters on the microstructure of plasma sprayed zirconias was studied analyzing SEM micrographs. The dependence of the coating composition on the structural features of plasma sprayed coatings is shown in Fig. 2.

The morphology of both samples is quite similar despite the different size and composition of started powder. There are a certain amount of pores and voids in the microstructures of as-deposited coatings. It was determined, that the distribution of structural elements in the microstructure of deposited coatings is quite homogeneous. Uniform and equal-sized grains are dominated in the structure of both groups of samples in spite of different sizes of precursor powders.

Table 2. Plasma spraying regimes for zirconia coatings deposition

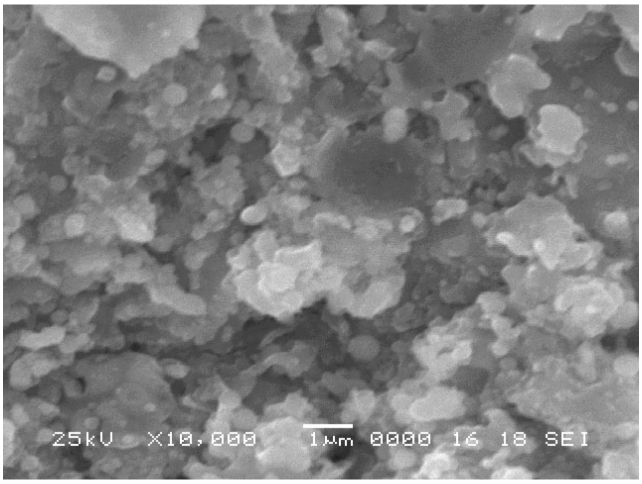
Spray regime	YSZ-1	YSZ-2
P, kW	47.7	49.4
G, gs^{-1}	5.2	4.33
v, ms^{-1}	1620	1145
T, °C	3320	3396
Spray distance, mm	70	70
Spray duration, s	20	20

The obtained coatings are nanostructured. The average grain size of plasma sprayed coatings estimated from SEM images is less 0.5 μm.

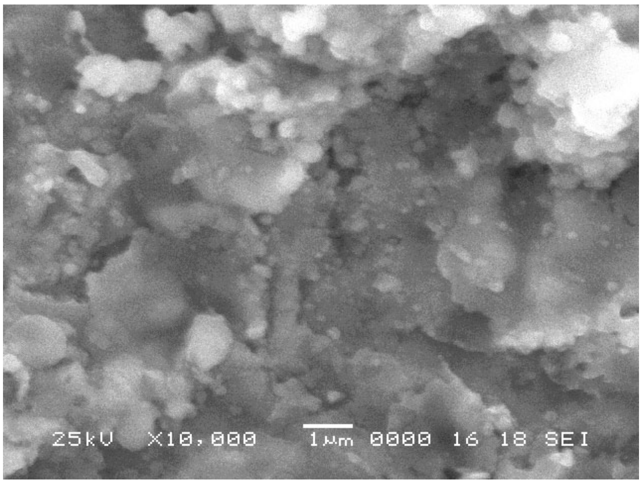
The phase composition of sprayed coatings YSZ-1 estimated from XRD diffraction patterns is the mixture of tetragonal, monoclinic and cubic phases. The analysis of peak positions in the XRD patterns of plasma-sprayed YSZ-2 zirconia indicated the presence of cubic phase dominated in the structure.

SEM analysis was used to evaluate the bonded interface adhesion of deposited coatings. Data of cross-sectional SEM analysis showed that sprayed coatings are well bonded to the substrates. Fig. 3 shows the cross-section views of polished samples of plasma sprayed zirconias deposited at the spraying parameters investigated. It may be seen that homogeneous distribution of particles and pores is typical over to the whole film thickness. The thickness of deposits is quite uniform and depends on spray duration. The thickness of ceramics deposits is in the range of 30 μm – 60 μm, when spray duration is 30 s and 60 s, respectively. The sprayed coatings are nanocrystalline. The average crystallite size, determined by the Scherrer equation [17] is 30 nm for YSZ-1 coatings and 27 nm for YSZ-2 coatings. For comparison, the crystallite size of as-sprayed plasma coatings from stabilized zirconia powder (0 μm – 50 μm in size) with 10 wt% yttria (Russian made) processed at 3330 °C is 33.8 nm [13].

The surface roughness, as important factor of tribological durability of the materials, was performed by profilometry based roughness analysis of sprayed coatings. The values of average roughness (*Ra*) and average maximum height of the profile (*Rz*) are presented in Table 3. The results of surface roughness measurements show, that the content of yttria does not have a great influence on the surface roughness parameters. Data of roughness measurements indicated that YSZ-2 coatings are slightly smoother than the coatings deposited using precursor with less content of yttria (YSZ-1).



a



b

Fig. 2. SEM micrographs of plasma sprayed zirconias YSZ-1 (a) and YSZ-2 (b)

Generally, the microhardness of the ceramic materials largely depends on the morphology and defect content [5]. A similar relation between microstructure and Vickers microhardness was observed for these plasma sprayed zirconia samples with analogous microstructures. The results of indentations made at 50 g loads (loading time 5 s) are presented in Table 3.

Table 3. Surface roughness parameters and microhardness values of plasma sprayed zirconias

Surface roughness parameter	Plasma sprayed coatings	
	YSZ-1	YSZ-2
Ra (μm)	2.64	1.37
Rz (μm)	14.97	9.52
Vickers microhardness $H\mu$, (MPa)	8342	9044
Hardness HRC	65	67

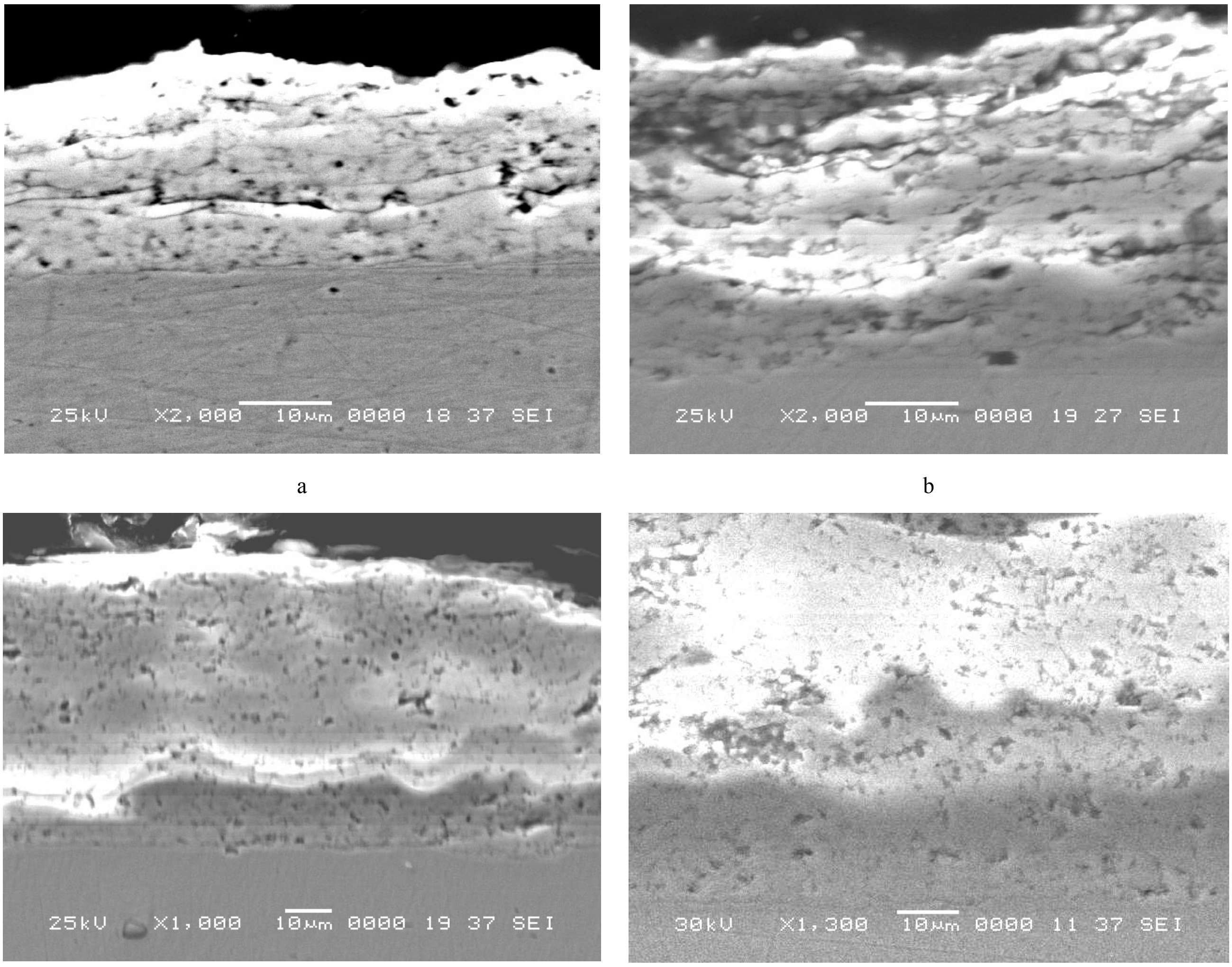


Fig. 3. SEM micrographs of cross-sectional area of polished plasma sprayed zirconias: YSZ-1 (a, c) and YSZ-2 (b, d)

The values of microhardness found to be quite similar for both groups of samples. Slightly lower surface roughness parameters and higher values of microhardness are attributed to plasma sprayed cubic zirconia. For comparison, the microhardness value of thermal barrier coatings of zirconia (7 wt% – 9 wt% Y_2O_3) processed by air plasma spraying [6] is 6.1 GPa at an indentation load of 50 g.

CONCLUSIONS

According to the results, it could be seen that the microstructure of YSZ coatings with 5.2 wt% and 10 wt% – 15 wt% yttria processed by atmospheric plasma spray technology is determined by plasma processing parameters. Yttria content does not have any substantial influence on the microstructure of plasma sprayed samples. The structural features, as well as surface roughness parameters are determined by processing technique.

The microhardness of plasma sprayed YSZ coatings is conditioned by the microstructure but not the composition of plasma-sprayed material.

Acknowledgments

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