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Thermal Treatment Influence on Microstructure of Plasma Sprayed Zirconia Thin Films

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The objective of the present study is to investigate the effect of heat treatment on plasma sprayed thin YSZ films deposited on the stainless steal sheets employing non-equilibrium plasma spraying technology at atmospheric pressure. Synthesized thin (20 – 30) μm samples of 10 vol% yttria stabilized zirconia (10-YSZ) for SOFC electrolyte application were thermally treated at temperature 800 °C for 1, 5 and 10 hours respectively.

Two different processing regimes with different processing temperature and their effect on coating microstructure and crystallinity has been investigated. Phase analysis of the plasma sprayed films by X-ray diffractometry (XRD) showed that the nano-scale particles were remained in the films after annealing. The analysis of the as-sprayed YSZ films showed the small increase of grain size during annealing.

Microstructure of polished cross-section of the as-sprayed and heat treated films has been investigated by scanning electron microscopy (SEM).

Keywords: films, microstructure, plasma spraying, ZrO_2, thermal treatment.

1. INTRODUCTION

Advanced ceramic coatings deposited by plasma spraying are used in large variety of industrial applications. The sprayed coatings are employed typically in industry to protect parts from severe conditions or to produce surface with specific function or properties [1].

At recent time plasma spray technology also is used for production of high quality thermoelectric materials [2]. This technology allows to make very thin layers, which results in improved performance and reduced material consumption [3]. Plasma spray processing offers a flexible and comparative simple and cheap way for producing SOFC electrodes or entire multiplayer SOFC [3, 4]. Fundamental researches have been carried out on manufacturing of YSZ electrode [1 – 2, 4]. It is very important, that the whole plasma spraying processes run at the same temperature and velocity, so SOFC layers do not need further thermal treatment [5].

Initial materials and mechanical properties such as microstructure, adhesion between SOFC layers and substrate and thermal resistance during long time operating at high temperatures determines SOFC lifetime [5, 6]. The major problem in the use of SOFC is the sampling of the deposited coatings due to the large thermal stresses produced during the thermal cycling [7, 8]. These stresses are induced mainly by the thermal expansion mismatch between ceramic coating layers as well as the temperature gradients within the coating and substrate [9].

The objective of this work was to examine the effect of annealing treatment on the properties and phase stability of thin YSZ films deposited on the stainless steel sheets employing non-equilibrium plasma spraying technology at atmospheric pressure. The films of stabilized zirconia with 10 wt% yttria (10-YSZ) were investigated.

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2. EXPERIMENTAL

Thin 10-YSZ films were deposited on the polished stainless steel sheets employing non-equilibrium plasma spraying technology at atmospheric pressure DC plasma torch. For this aims a special test bench with linear single – chamber plasma torch was built [10]. Continual date monitoring of operating plasma torch allows the test bench functioning. Schematic view of the experimental set-up is shown in Fig. 1.

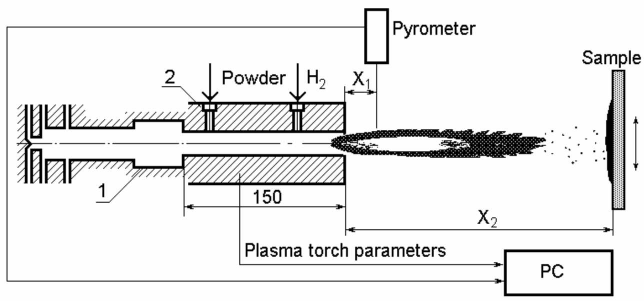


Fig. 1. The scheme of experimental set-up: 1 – plasma spray gun, 2 – reactor, X_1 – the distance to outlet particle temperature measurement place, X_2 – sample location distance

The operating parameters of the plasma torch: power supply (P) – 35 – 40 kW, arc current (I) – 120 – 200 A, voltage (U) – 225 – 300 V, total gas flow rate (G) – 4.9 gs^{-1} (the main gas flow rate through plasma torch – 2.65 gs^{-1}, additional – 2.25 gs^{-1}, hydrogen – 0.15 gs^{-1}). Powder injection was provided into reactor, which was connected directly to plasma torch anode. Such construction permits continuance-injected powder in high temperature plasma core for longer time and provides better melting conditions. Outlet powder temperature was controlled by pyrometer.

Stabilized zirconia powder (0 – 50 μm in size) with 10 wt% yttria was used for plasma spray deposition. Plasma spraying was done in two regimes with different amount of H_2. The hydrogen gas is added to increase the heat content of the flame and thereby the power of the system. This enables high melting point ceramics to be melted. Average plasma temperature in the powder injection place was 3300 – 3700 °C, outlet plasma temperature – 3000 – 3300 °C, the average velocity – 650 – 1350 ms^{-1} and the working gas – air. Table 1 summarizes the experimental conditions.

Table 1. Plasma spraying regimes for YSZ films deposition

Regime	1	2
P, kW	47.75	47.75
G, g/s^{-1}	4.3	4.3
$G(H_2)$, g/s^{-1}	0.1	0.15
T, °C	3330	3585
X_2, mm	70	70
Coating time, s	30	30

The deposited samples were heat treated in the furnace *SNOL* 1,6.1/11 – *I*2 at 800 °C (SOFC working temperature) for 1, 5 and 10 hours respectively. The heating rate was 11 °C/min. The temperature was controlled by platinum thermocouple, which was placed near the sample surface.

Scanning electron microscopy was used to examine the microstructure evolution of the films. Polished cross-sections of the samples were prepared for scanning electron microscopy (SEM). All specimens were investigated using JSM 5600.

After heat treatment the samples were characterized by X-ray diffraction (DRON-6 with Cu K_α-radiation). The mean crystallites size was estimated from integral breadths of the diffraction peak (111) of YSZ by WINFIT program [11].

The film thickness was evaluated by cross-sectional scanning electron microscopy (SEM) observation. The specimens for cross-sectional microscopy were prepared by mounting the samples in epoxy resin, followed by polishing through 0.05 μm alumina.

3. RESULTS AND DISCUSSION

The XRD patterns as a function of the annealing duration of the treated film are given in Fig. 2. According to this the crystalline phase of as sprayed films is attributed to the cubic phase. For our composition (10-YSZ), a (*c* + *t*) two-phase system would be expected [12]. The existence of tetragonal symmetry phase with *c/a* ratio very close to 1 was checked using conventional XRD by detail detecting of second phase appearance from broadening and splitting up of (200) and (400) cubic reflections. In all cases the tetragonal symmetry was not found indicating a pure cubic system. The as-sprayed layers were further treated in the furnace for 1 – 10 hours, which not resulted in a change in phase development, but in a marginal growth in crystallite size (Fig. 3). There is no new phase, except one peak, attributable to the substrate (Fig. 2 a, 2 curve), and no clear difference of the peak intensities between them. Both the as-sprayed and preheated films are composed of pure cubic zirconia. The absence of any reflections from the substrate material indicates a continuous and thick deposit of YSZ [13].

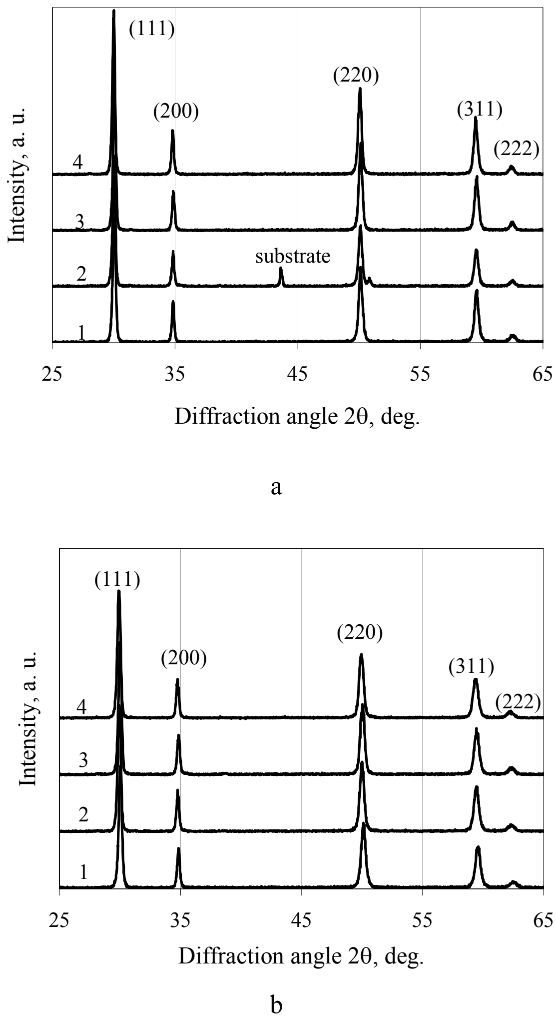


Fig. 2. The XRD patterns of YSZ films: a) plasma sprayed by regime 1 and b) sprayed by regime 2: 1 – as sprayed films, 2, 3, 4 – the post treated films. The treatment duration: 2 – 1 h, 3 – 5 h, 4 – 10 h

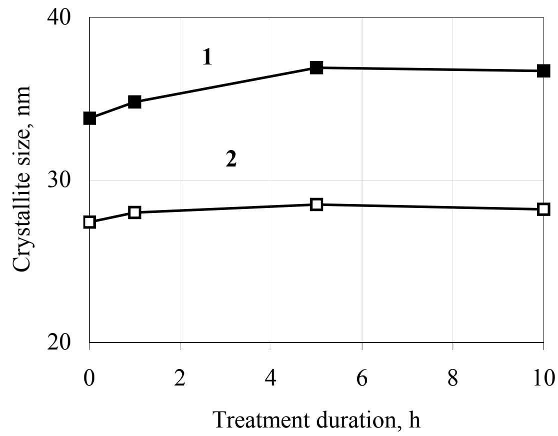
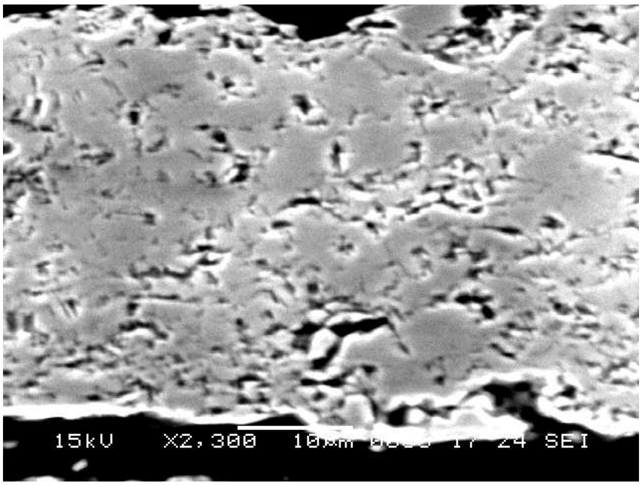
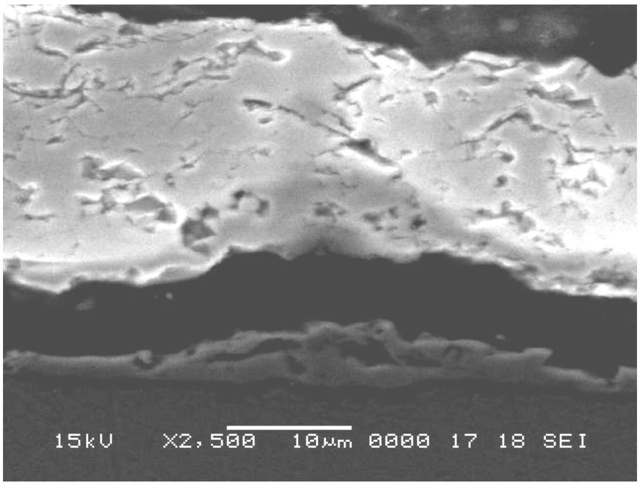


Fig. 3. Effect of plasma-spay regime and heat treatment duration on crystallite size of as-sprayed and treated zirconia films: 1 – regime 1 and 2 – regime 2

The crystallite size of the as sprayed films deposited by regime 1 is 33.8 nm (Fig. 3), while the crystallite size of the films sprayed by regime 2 (*T* – 3585 °C) is 27.4 nm. The crystallite size of the films after heat treatment at



a



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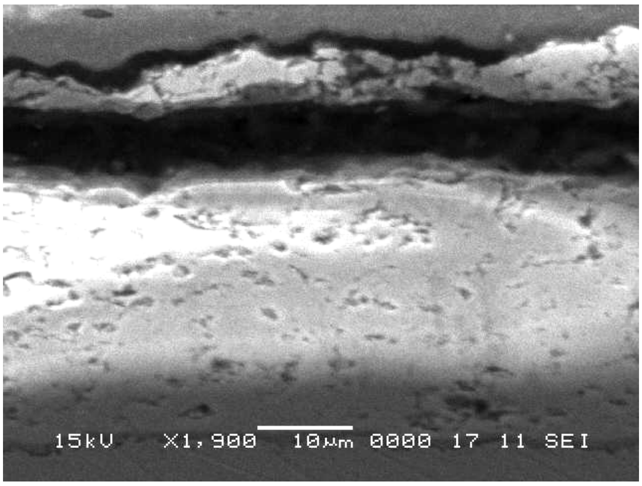

c

Fig. 4. SEM micrographs of plasma sprayed YSZ films deposited by regime 1: as sprayed (a) and heat treated at 800 °C for 5 hours (b) and 10 hours (c)

800 °C for 10 hours is not very differing from the as sprayed films and increases up to 28.3 nm for samples deposited by regime 2 and to 36.8 nm for films sprayed by regime 1, respectively. The increase of heat treatment time from 5 to 10 hours does not affect significantly the crystallite size (Fig. 3).

The present study shows the influence of spray regimes and heat treatment conditions on the changes of the structure of the YSZ films. Figure 4 and Figure 5 show SEM micrographs of the as-sprayed and post-treated zirconia films. Despite different spraying regimes, the morphology of both films is similar, as shown in Fig. 4 a and Fig. 5 a. Randomly distributed pores of different sizes are observed in the films micrographs.

By the data obtained, the microstructures of the heat-treated films at 800 °C temperature (Fig. 4, b and c and Fig. 5, b, c and d) do not change significantly when compared to the as-sprayed condition of investigated samples (Fig. 4, a and Fig. 5, a). From the SEM analysis, it was observed, that heat treatment causes changes in the amount and shape of porosity due to grain growth and sintering. The material becomes denser. Pores agglomerate during heat treatment. Post treated films are qualified by finer and reduced porosity and increased density (Fig. 4, c) and Fig. 5, d).

This indicates that although some growth of nano grain took place, it is not very rapid during the annealing process and the film remains nanostructured.

A scanning electron microscopy was used to determine the films morphology and their thickness. The average film thickness evaluated by cross-sectional SEM observation was from 35 μm for as sprayed zirconia film deposited by regime 1 to 47 μm for as sprayed film deposited by plasma spraying regime 2.

4. CONCLUSIONS

In this study, nanostuctured zirconia films are deposited employing non-equilibrium plasma spraying technology at atmospheric pressure.

The present study showed the data of phase analysis and the structural changes of the plasma sprayed YSZ films after heat treatment at 800 °C with increasing the time duration from 1 hour to 10 hours.

By the data of the XRD analysis no distinct peaks except for cubic YSZ are found from XRD patterns of as sprayed and heat treated zirconia films. During thermal treatment the crystallite size increases marginally with increase of annealing duration from 1 hours to 10 hours.

No substantial changes in the films microstructure were observed after the thermal annealing. The data indicate that the regime of thermal treatment of films does not significantly affects the structure of YSZ films. It was observed, that heat treated films are qualified by finer and reduced porosity and increased density.

Based on the results obtained, it can be deduced, that the annealing of YSZ films at 800 °C temperature for 10 hours has a marginal influence on the structural changes and no influence on the phase content of these films.

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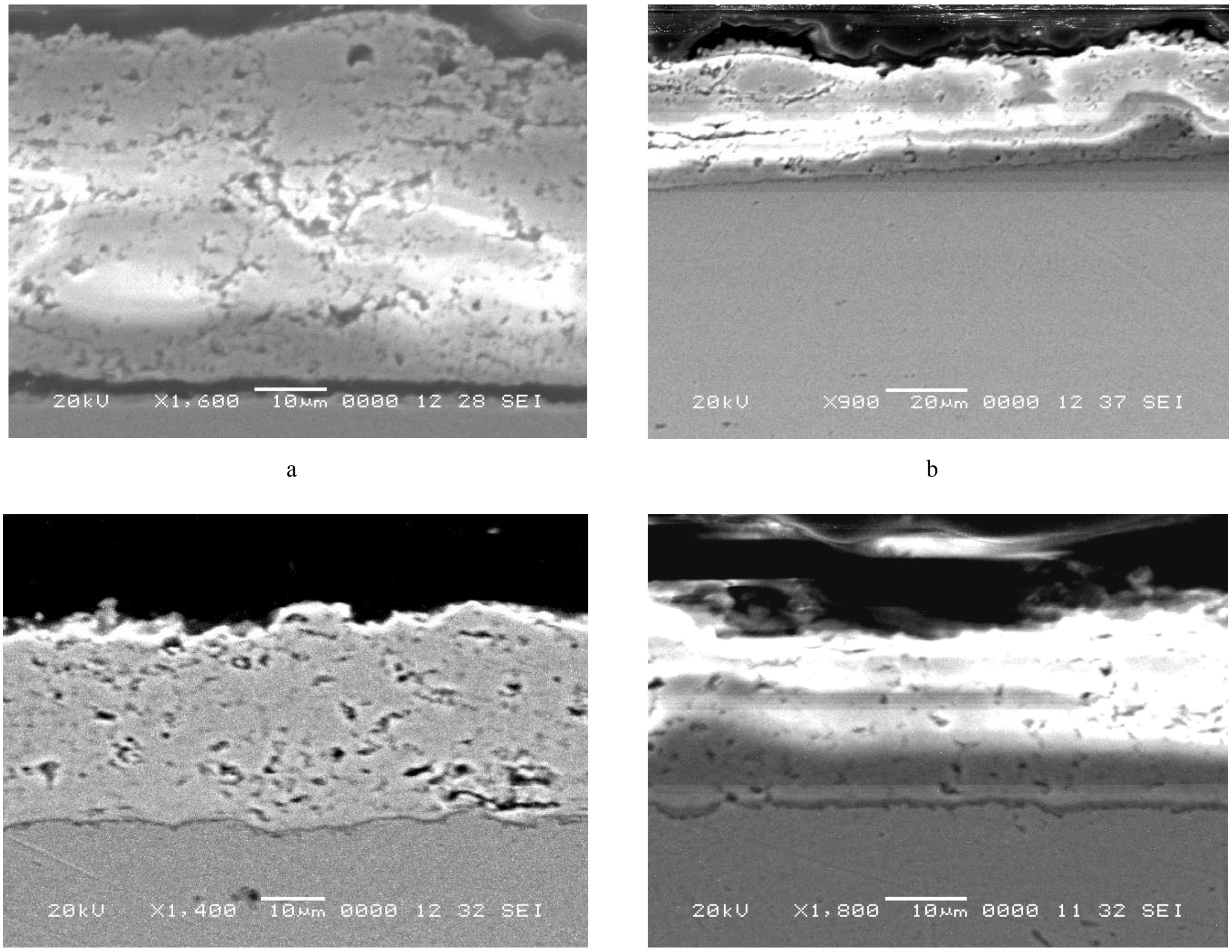

Fig. 5. SEM micrographs of the plasma sprayed YSZ films deposited by regime 2: as sprayed (a) and heat treated at 800 °C for 1 hour (b) 5 hours (c) and 10 hours (d)

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