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Investigation of Plasma Coatings Manufactured from Synthesized Zirconia

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This paper studies the influence of feedstock material characteristics on the plasma coating properties. Yttria-stabilized zirconia (YSZ) coatings with the thickness up to 60 μm were prepared by plasma-spray technique on the stainless steel substrates employing non-equilibrium plasma spray technology at atmospheric pressure. The precipitation method has been used to prepare precursor ceramic powder. The characteristics of synthesized powders and sprayed samples were evaluated depending on the calcination temperature of synthesized initial powder. The data of scanning electron microscopy (SEM) revealed uniform fine-grained microstructure with grain size < 0.5 μm. The cubic phase with nano-sized crystalittes has been found to dominate in the plasma sprayed coatings.

Keywords: ceramic powder, YSZ, plasma spraying, coating, microstructure.

INTRODUCTION

Engineering ceramics are ideally suited materials for high performance applications because of the combination of such properties as wear resistance, hardness and corrosion resistance [1]. The products made from engineering ceramics are wear resistant and long lasting.

High temperature oxide ceramics based on zirconium oxide exhibit excellent properties and are widely used as an important multifunctional material due to high heat resistance, high mechanical strength at high temperatures, low and constant thermal conductivity at a large temperature region, high oxygen conductivity, etc. [2–4]. This is one of the several reasons for regarding yttria-doped zirconia (YSZ) as a promising reference material for thermal conductivity measurements at higher temperatures [5]. Yttria stabilized zirconia is technologically important material generally used for solid electrolyte in fuel cell systems operating at a high temperature of ~1000 °C [6–8]. Zirconia based coatings are widely used as thermal barrier coatings in high-temperature engine components to enable higher operating temperatures [9–10]. Zirconia doped with 8 mol% –10 mol% yttria is characterized by higher ionic conductivity at 850 °C–1000 °C [7]. At low temperature the ionic conductivity of this material decreases.

The structural features are reliant on material properties and mechanical behaviour of the ceramics and ceramic coatings. Structure is the keystone for understanding and studying the properties of the ceramic materials. Many investigations of the properties of structural and functional ceramics declare the importance of processing on the final properties of the ceramic – starting with the synthesis of initial powder to the fabrication of final ceramics [11–13]. Most of the works concentrate on the changes of specific properties with the changes of type and amount of stabilizer, processing methods and parameters, sintering characteristics, etc. [11, 12]. Heat treatment may induce the sintering of the material, grain growth and the changes of the porosity. The electrical properties are strongly dependent on the structural characteristics of the material and the test conditions [7, 8].

These ceramic materials can be processed using a wide range of manufacturing methods. The manufacturing process of the ceramics that starts with the processing of precursor powders affects the morphology and microstructure of the materials [14]. The started powder properties affect the properties the materials and can be improved using non-conventional methods of powder synthesis (co-precipitation, hydrothermal, sol-gel, etc.) allowing the preparation of uniform, nano-sized and highly reactive powders [13, 15]. Many methods are employed to prepare YSZ powders and every method has its own advantages and disadvantages. Conventional ceramic powder processing requires a lot of stages, including long-lasting mixing, milling, drying and finally high temperature calcinations. Wet chemical synthesis is very simple and can lead to powders with desirable characteristics [16]. Wet synthesis methods have many advantages over conventional ceramic powder synthesis methods: low costs of instrumentation and energy, direct fabrication of crystalline materials at low synthesis temperatures, utilization of low cost inorganic precursors – water-soluble salts, nano-scale crystallite size of obtained powders, good chemical and structural homogeneity, high purity, etc. [11, 17]. In order to obtain homogeneous and nanosized YSZ powder several methods of synthesis are developed [17–19].

The microstructure and properties of ceramic coatings are closely linked to the processing technology similarly [9]. Different thermal spraying methods are used to form ceramic coatings on different substrates. Plasma spraying is one of the most accessible and low-cost deposition techniques [20]. Plasma process parameters and the properties of feed stock material influence the microstructure and film adhesion of coatings [21]. The results show that the grain-boundary conductivity of plasma-sprayed yttria-zirconia increases with decreasing precursor particle size [22]. The feedstock powder characteristics also strongly affect the particle state in plasma and the resultant coating properties [23]. Small particles are shown to melt more

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completely in the plasma flow. Thermally sprayed ceramic coatings deposited from nanostructured feedstock powder possess improved properties in comparison to the coatings produced from conventional powders [24]. In contrast with spraying conventional powders, complete melting of the nanostructured raw stock is to be avoided [25]. This type of coating has been reported to exhibit better wear resistance and higher adhesion strength compared with conventional deposits. Powder consisting of spherical particles has been reported to produce coating with lower unmelted particles and lower thermal conductivity [25].

The results reported in this study represent the structural data of plasma sprayed zirconia coatings prepared from yttria stabilized zirconia powders synthesized by precipitation method. The relationship between the started powder characteristics and the structural data of plasma sprayed coatings has been studied.

EXPERIMENTAL

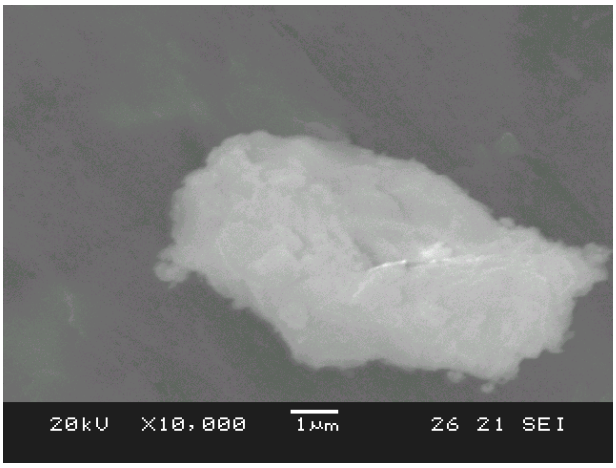
The initial zirconia powders were obtained by co-precipitation of aqueous solutions of zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8\,H_2O$) and yttrium nitrate hexahydrate ($Y(NO_3)_3 \cdot 6\,H_2O$) (mixed in the ratio 90:10) by ammonia solution to keep the process at pH = 9.0 to 9.5 [26]. The dehydration and crystallization behavior of powders was analyzed by differential thermal analysis (DTA) and XRD techniques. The obtained YSZ powders were used for preparation of plasma sprayed specimens.

Plasma sprayed coatings were deposited employing the non-equilibrium plasma spraying technology at atmospheric pressure [29], suitable for various engineering applications. The experimental procedure, equipment and operating conditions have been described in [29]. Stainless steel substrates were used for the deposition of YSZ. 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 the reactor exit and fixed on a cooled plate. The coatings were formed moving the plasma torch in a horizontal direction. The thickness of the substrates was 1.2 mm.

The synthesized powders and plasma sprayed samples were characterized by XRD employing a DRON-UM1 diffractometer with Cu anode K_α radiation for identification of existing phases. Crystallite size of the zirconia powders and coatings was estimated from Scherrer's equation. SEM (JEOL JSM 5600) analysis was performed for evaluation of structural features and morphology of zirconia powders and sprayed coatings.

RESULTS AND DISCUSSION

The precipitated powders were washed repeatedly with distilled water to remove chlorine ions (no trace of Cl^- by silver nitrate test). The hydrolysis product, hydrous zirconia-yttria hydroxides, was freeze dried at –15 °C for 12 h to prevent the formation of large particle aggregates [27, 28]. Figure 1 shows SEM images of YSZ powder synthesized by precipitation method and calcined at 1000 °C for 0.5 hours. The particle size and shape of synthesized powders is quite uniform.



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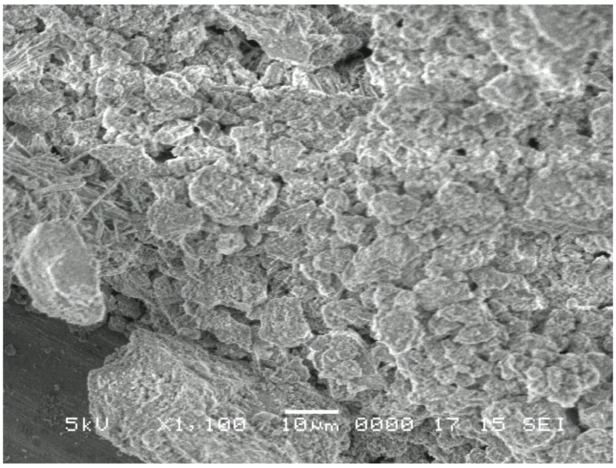

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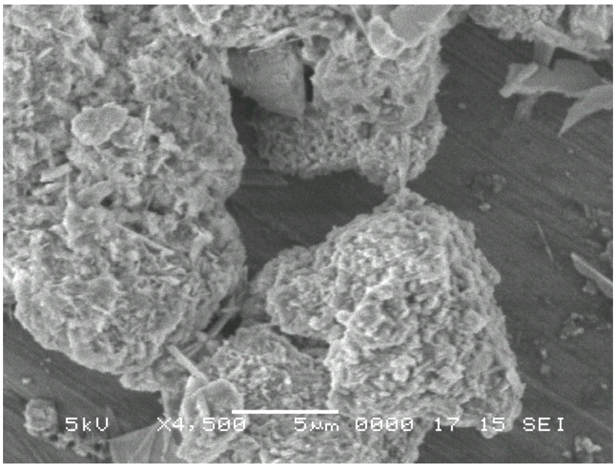


c

Fig. 1 Typical SEM views of as-synthesized YSZ powder (a) and calcined at 1000 °C for 0.5 h (b and c)

The synthesized powder obtained from aqueous solutions of metal salts is weakly aggregated in aggregates of nanoparticles that appears to be similar to conventional ceramic powders. The typical size of aggregates is ~10 μm.

The synthesized powders were dried at 80 °C, crushed and calcined to form oxide powder. The crystallization temperature was determined from DTA data. The exothermal effects in the temperature range from 460 °C to 500 °C are referable to crystallization process of amorphous hydroxide crystalohydrates. The hydrous gels were calcined at 500 °C and 1000 °C to insure the crystal

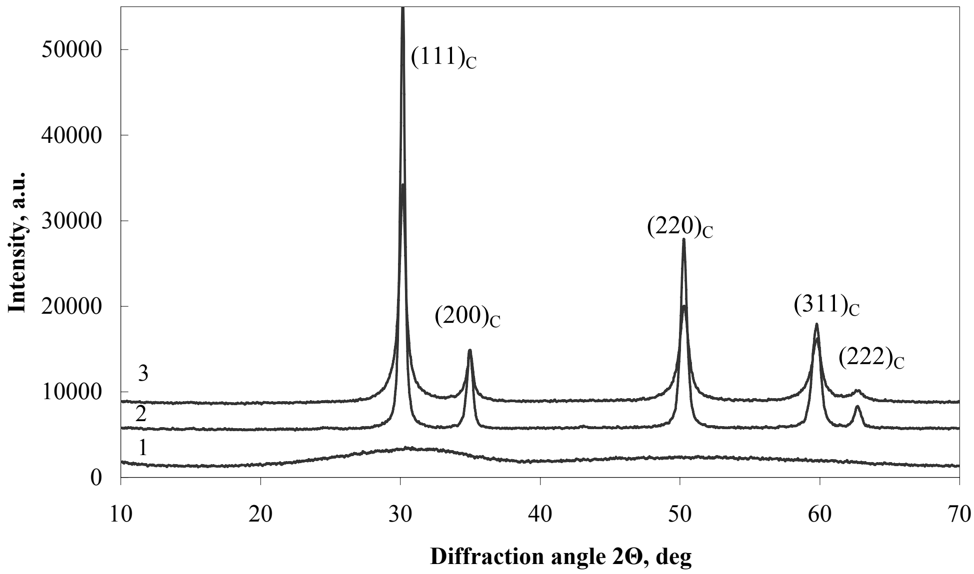


Fig. 2. XRD patterns of synthesized YSZ powders: 1 – hydrous zirconia dried at 80 °C, 2 – YSZ-1 powder calcined at 500 °C and 3 – at 1000 °C. Calcination time 0.5 h

phase stability. The results of XRD analysis are presented in Table 1. According to the data of XRD analysis as-precipitated hydrous zirconia powder is amorphous. Figure 2 shows diffraction profiles of the synthesized powder calcined at different temperatures. After the calcinations at 500 °C and 1000 °C temperatures for 0.5 hour the powders are crystalline materials composed from cubic phase of zirconia. The analysis of XRD patterns of calcined powders in the range of 2θ angles of 25°– 65° showed that only cubic phase reflections dominate in the diffractograms (Fig. 2, Table 1). The higher calcination temperature does not change the crystal orientation of obtained powders, only the intensity of peaks increases with increasing the calcination temperature of the material. The intensity of (111) peak increases nearly twice for YSZ powder calcined at 1000 °C. The peaks corresponding to monoclinic phase do not appear in the patterns of any of the calcined powders.

The crystallites size was calculated from XRD patterns according to Scherrer's equation using the (111) diffraction peak of cubic zirconia. The average values of crystallites size are presented in the Table 1. The powder calcined at higher temperature is characterized by larger crystallite size.

Two groups of zirconia coatings were plasma processed on steel substrates using the synthesized powders YSZ-1 and YSZ-2. Table 2 presents the characteristics of the started powders investigated in the present study and main plasma process parameters.

The crystal orientation of plasma sprayed samples YSZ-1 is the same as precursor powder – cubic (Fig. 3). Cubic phase is dominant in the XRD pattern of the sample YSZ-2 too. But in this case, some amount of cubic phase transforms into monoclinic phase during plasma spraying. A peak (111) of low intensity at the diffraction angle 28 deg, attributable to monoclinic zirconia, was detected in this XRD pattern.

The obtained coatings are nanostructured. The average crystallites size, calculated from higher intensity peaks by the Scherrer's equation is 35 nm for plasma sprayed coating YSZ-1. In the case of YSZ-2, the crystallite size is 33.1 nm of cubic phase and 12.2 nm for monoclinic zirconia.

Table 1. Crystal structure of the synthesized YSZ powders

Powder	Calcination temperature, °C	Crystal structure	
		Phase	Crystallite size, nm
YSZ-1	500	Cubic	13.3
YSZ-2	1000	Cubic	24.2

Table 2. Plasma spray parameters and started powder for YSZ coatings deposition

Spray regime	Started powder	
	YSZ-1	YSZ-2
P, kW	47.34	46.22
G, gs^{-1}	5.45	5.42
v, ms^{-1}	1430	1428
T, °C	3220	3210
Spray distance, mm	70	70
Spray duration, s	15	15

Effect of spraying parameters on the microstructure of plasma sprayed zirconias was studied analyzing SEM micrographs (Fig. 4). The morphology of both samples is quite similar despite the different calcination temperature of the synthesized powder. Uniform and equal-sized grains dominate in the structure of both groups of samples in spite of different calcinations of precursor powders. The average grain size estimated from SEM images of plasma sprayed coatings estimated from SEM images is less 0.5 μm. The distribution of pores and voids is quite homogeneous. As-sprayed coatings manufactured from synthesized powders

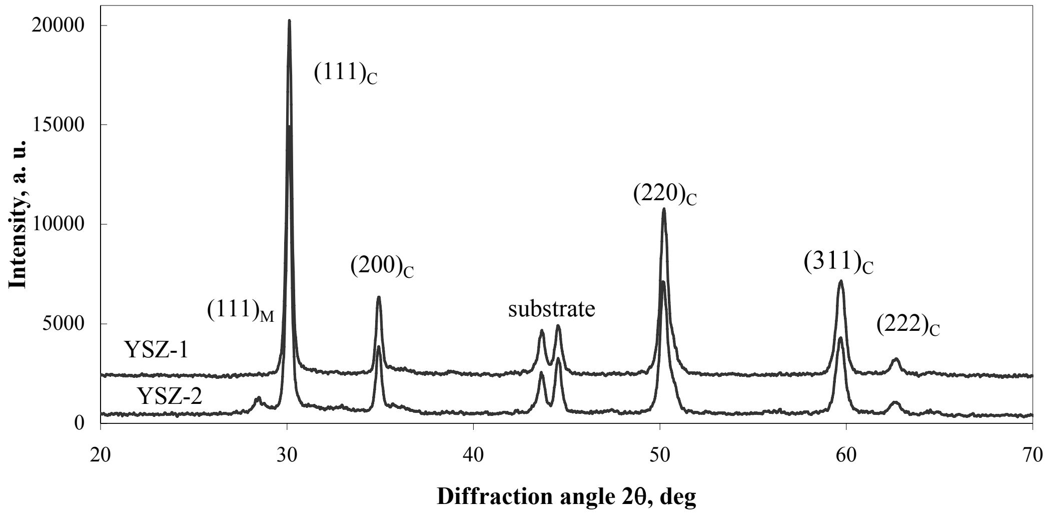
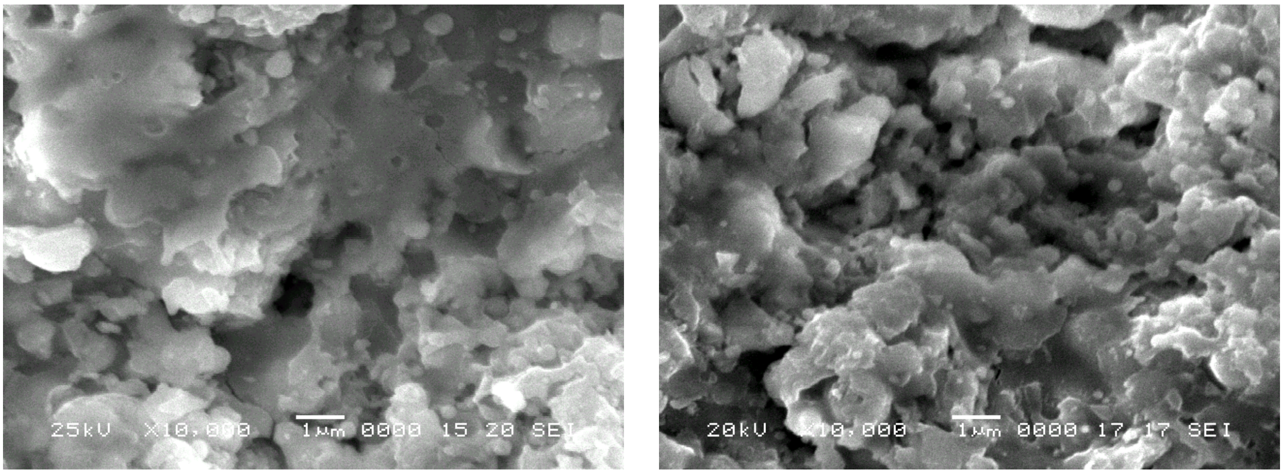


Fig. 3. XRD patterns of YSZ coatings plasma sprayed from 1 – YSZ-1 powder and 2 – YSZ-2 powder



a b

Fig. 4. SEM micrographs of plasma sprayed zirconias YSZ-1 (a) and YSZ-2 (b)

are qualified by finer and reduced porosity and increased density in comparison with the coatings from conventional YSZ powder [29]. The thickness of sprayed samples evaluated from the cross-sectional SEM observation is about 60 μm.

CONCLUSIONS

Homogeneous nanocrystalline YSZ powders with cubic structure were synthesized by simple precipitation method from low cost precursors. The powders produced are in the form of agglomerates of about 10 μm. After calcination at 500 °C and 1000 °C temperatures the average crystallites size values are 13.3 nm and 24.2 nm, respectively.

Plasma sprayed coatings with high relative density and fine-grain structure were obtained from the synthesized powders. Cubic phase alone has been found to exist in the plasma sprayed coatings prepared by atmospheric plasma spray technology from synthesized powder calcined at lower temperature. According to the data, the better results were obtained using precursor powder calcined at 500 °C. The calcination temperature has no substantial influence on the crystallite size of prepared coatings. According the results, the produced powders are perspective precursor material for the preparation of plasma sprayed YSZ coatings with cubic crystal orientation.

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