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Dielectric Strontium Zirconate Sprayed by a Plasma Torch

P. Ctibor[1, 2*], J. Sedlacek[2], M. Janata[3]

1. Institute of Plasma Physics, ASCR, Za Slovankou 3, 182 00 Praha 8, Czech Republic.

2. Department of Electrotechnology, Faculty of Electrical Engineering, Czech Technical University, Technicka 2, 166 27 Praha 6, Czech Republic.

3. Chief of the LPT dislocated laboratory, Institute of Plasma Physics, ASCR, Za Slovankou 3, 182 00 Praha 8, Czech Republic.

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ABSTRACT

A multifunctional material, strontium zirconate, $SrZrO_3$, studied in literatures as a dielectric ceramics, thermal barrier coating, proton-conductor, and luminescent material was sprayed by a water-stabilized plasma torch WSP 500. Stainless steel and plain carbon steel were used as substrates. Coatings with thickness of 1 to 2 mm were produced, whereas the substrates were preheated over 450 °C. The torch working at 150 kW was able to spray $SrZrO_3$ with a spray rate of 10 kg per hour. Microstructure, phase composition, dielectric properties, and optical band gap were also investigated. Prog. Color Colorants Coat. 10 (2017), 225-230© Institute for Color Science and Technology.

1. Introduction

Detailed investigation of phase transformations was done on $SrZrO_3$ produced using metal chelates as starting materials [1]. $SrZrO_3$ should exhibit a volume change due to a phase transition from orthorhombic to pseudotetragonal phase at 730 °C and for this reason, it was tested as thermal barrier coating (TBC) preferably not in pure state but with dopants like Yb_2O_3 and Gd_2O_3. The study of Hasegawa et al. [1] revealed the second-order phase transition with ΔCp of 8 J/mol K from orthorhombic distorted perovskite with the space group Pbnm (No. 62) to a new phase with Ibmm space group (No. 74) at 769 °C. By further heating, the orthorhombic perovskite with Ibmm (No. 74) changed to tetragonal one with the space group of I4/mcm (No. 140) by the first-order phase transition with ΔH of 58 J/mol at 848 °C. At 1102 °C, the crystal symmetry changed to cubic with the space group of Pm-3m (No. 221) by the second-order phase transition with ΔCp of 5 J/mol K. The endothermic peak was detected at 769 °C on DTA curve also by authors of another work [2].

A non-conventional but prospective production technique for ceramic dielectrics is plasma spraying [3]. Investigation on the sprayed $SrZrO_3$ [4] indicated that the coating microstructure, porosity and deposition efficiency could be correlated with the torch input power and spray distance in terms of the particle temperature and velocity. Porosity varied from 8 % for high torch power to 37 % for low torch power. Maximum microhardness was about 2.75 GPa for the high torch power. Plasma spraying of $SrZrO_3$ was carried out also by other type of gas-stabilized plasma torch [5] and by a special high feed-rate three-cathode plasma torch [6].

*Corresponding author: ctibor@ipp.cas.cz

Medium-size (10–50 nm) intragranular pores (studied by small angle neutron scattering, SANS [6]) sintered during a thermal exposure. The in situ SANS revealed that this process starts at 1000 °C. A creation of nanopores starting at 900 °C was detected in the $SrZrO_3$ layer. These nanopores began to disappear at 1100 °C.

Dielectric properties of strontium zirconate are also reported. $SrZrO_3$ thin film prepared by metal-organic decomposition technology followed by annealing at 700 °C [7] exhibited relative permittivity of 30 and the loss factor of 0.005, both well stable upon changing the frequency between 100 Hz and 10 MHz. Layer formed from a nanosized $SrZrO_3$ [2] exhibited relative permittivity of about 260 at 1 kHz (with loss factor of about 0.30) and about 140 at 1 MHz (loss of 0.04). The same paper reports that the value of band gap is about 5.6 eV (assuming indirect transition of electron from valence to conduction band). The same value of band gap is reported also elsewhere [8].

The aim of our paper is to spray strontium zirconate by a high power and high heat flux torch and study the dielectric properties, whereas also microstructure aspects and mechanical aspects were treated as important for the overall coating character.

2. Experimental

2.1. Feedstock and spraying

Plasma spray grade strontium zirconate powder supplied by Cerac Inc. (Wisconsin, USA) was used as the feedstock. The powder particle size was 74 to150 μm. Plasma spraying was done by the WSP torch [9, 10] at 150 kW (500 A, 300 V). The feeding distance was set to 80 mm and spray distance was 350 mm. Compressed air was applied as the feeding gas and the substrates were preheated to 460 °C. After each pass of the torch, the temperature rose to 350 °C and was turned down to 170 °C by a compressed air flux before starting the next pass. Stainless steel as well as carbon steel coupons was used as substrates. High substrate preheating was used based on our experience; dielectric properties of titanate perovskites could be improved by this factor [9]. The two substrate materials were used to examine the influence of substrate oxidation on electrical properties of the coating-substrate system.

2.2. Characterization techniques

Polished cross sections of the coatings were prepared for microscopic observation and for microhardness measurement. The resolution of light microscopy is sufficient to visualize the interlamellar pores but not the ultra-fine vertical cracks that are also common in plasma sprayed coatings [11]. Microhardness of the coatings was measured on cross sections on an optical microscope equipped with a Hanemann head and Vickers indenter using a 1 N load applied over 15 seconds. The mean value of microhardness was calculated as an average of 20 indentations.

The coating's phase composition was analyzed by powder X-ray diffraction (PXRD) with $Cu_{K\alpha}$ radiation. D8 Discover diffractometer (Bruker AXS, Germany) equipped with 1D detector Lynxeye (Bruker AXS, Germany) was used in divergent beam geometry. Moreover, the obtained PXRD patterns were subjected to Rietveld refinement in order to ascertain the weight fraction of the identified phases, refine their lattice parameters and calculate the average values of coherently scattering domains (CDD) reflecting the so-called crystallite size.

Electrical measurements were performed on the coatings adhered on the metallic substrate. The surface of specimens was ground to eliminate surface roughness. Layers of aluminum as thin film electrodes were sputtered under reduced pressure on the topside of each sample. A three-electrode measurement fixture was used to evaluate dielectric parameters of the samples. The electric field was applied parallel to the spraying direction (i.e., perpendicular to the substrate surface). Capacity was measured in a frequency range from 5 kHz to 1 MHz using a programmable impedance analyzer (4284A, Agilent, USA). Applied voltage was 1V AC [12]. Relative permittivity ε_r was calculated from measured capacity C_P and specimen dimensions since ε_r is directly proportional to C_P according to the Eq. 1.

$$C_P = \varepsilon_0 \times \varepsilon_r \times S/k \quad (1)$$

where $\varepsilon_0 = 8.854\times10^{-12}$ F m^{-1} and S/k [m] is defined as the ratio between the guarded surface and the thickness of the sample. This technique is accurate enough ($C_P \pm 0.01$ pF) for dense materials (over 95 % of the theoretical density) [13]. The same arrangement and equipment were used for the loss tangent measurement at the same frequencies as capacity.

Electric resistance was measured with a special resistivity adapter – Keithley model 6105. The electric field was applied from a regulated high-voltage source and the values were recorded by a multi-purpose electrometer (617C, Keithley Instruments, USA). The applied voltage was 100 ± 0.05 V DC and the exposure time of 10 min. Volume resistivity was calculated from the measured resistance and specimen dimensions.

The diffuse reflectance was measured by an UV-VIS-NIR scanning spectrophotometer (Shimadzu, Japan) with a multi-purpose large sample compartment. The reflectance curves obtained between 400 and 2000 nm were then converted to absorbance and recalculated [14] to the bandgap energy E_{bg}.

3. Results and Discussion

Microstructures of the as-sprayed coatings are shown in the Figure 1. Archimedean (water immersion) specific weight was 4.5372 g/cm^3. Microhardness is summarized in Table 1. In the near-substrate region (about 40 µm distant from the substrate), the coating sprayed on carbon steel is harder. Reported values for several sprayed $SrZrO_3$ coatings [4] vary in a broad range whereas our coatings are in the middle of the interval.

Spherical pores are more advantageous for mechanical as well as dielectric homogeneity and isotropy. The XRD pattern, Figure 2, indicates the presence of phases with tetragonal and orthorhombic symmetry. Due to the similarity of peak positions (i.e. lattice plane distances), and intensity ratios, the tetragonal phase is isomorphous with tetragonal zirconia (t-ZrO_2) stabilized at room temperature. The orthorhombic distorted perovskite phase is the most stable one at low temperatures; from this viewpoint, we can describe the coatings as relatively slowly quenched, and it is due to high substrate preheating before spraying.

Table 1: Mechanical and thermal parameters, electric resistivity.

Microhardness-total	[GPa]	Microhardness [GPa]	Resistivity [Ohm m]	E_{bg} [eV]
on stainless steel	5.53 ± 2.18	near substrate 5.58 ± 1.30	2.84E8	3.6
on carbon steel	5.62 ± 2.62	near substrate 8.01 ± 1.24	9.53E7	3.6
Ref [4]	2.8 and less	-	-	-

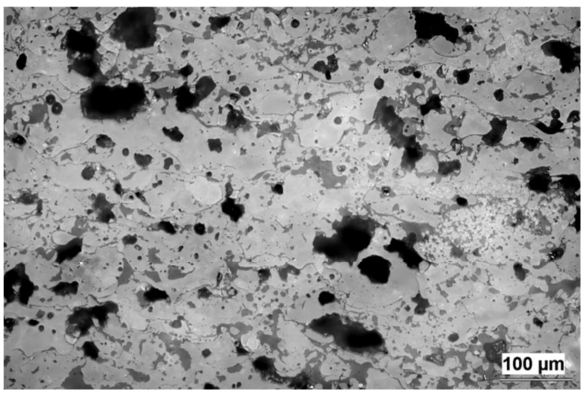

Figure 1: Cross sections of the $SrZrO_3$ coating, light microscopy.

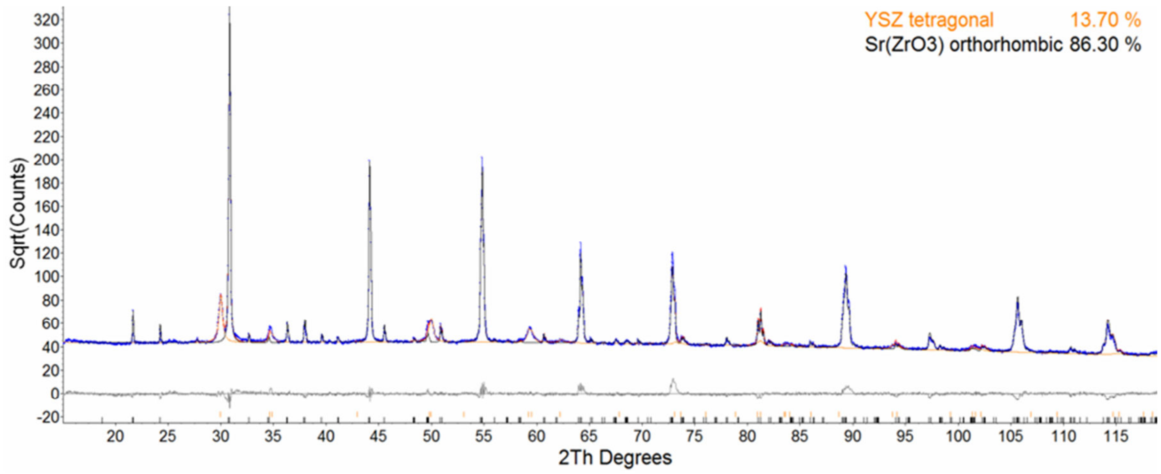

Figure 2: XRD pattern of plasma sprayed $SrZrO_3$.

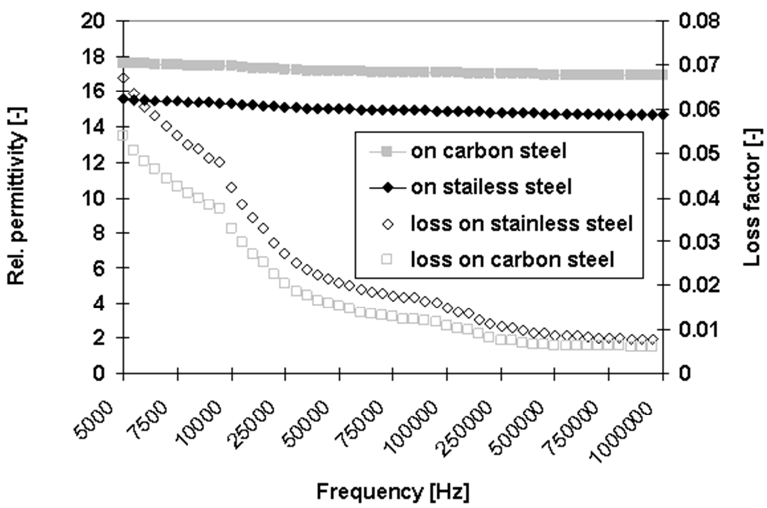

Figure 3: Relative permittivity and loss factor of plasma sprayed $SrZrO_3$.

Dielectric properties are illustrated in Figure 3. The coating sprayed on carbon steel has higher relative permittivity and in the same time lower loss factor, i.e. it is slightly a better dielectric ceramics (particularly from the capacitor viewpoint). Values of permittivity and loss factor are similar for both coating substrates and also the run versus the changing frequency has exactly the same character. In another work [7], the permittivity values were between 22 and 30 (frequency interval of 100 Hz to 100 MHz) and the loss factor values were between 0.01 and 0.02. The samples exhibited lower permittivity and higher losses at low frequencies due to the high porosity and non-perfect homogeneity. The porosity is always disadvantageous for the dielectric performance. Our coatings, however, have lower losses at frequencies above 200 kHz than the previously reported values [7]. For plasma sprayed $SrZrO_3$ coatings, the dielectric data are absent in the open literature.

Strontium zirconate is, as many ceramics, sensitive to low-frequency polarization (manifested itself by high permittivity and high loss) and its magnitude depends critically on the manufacturing technology or thermal history, i.e. on microstructure formed due to it. Our $SrZrO_3$ coating is porous and does not fit well the requirement for precision of permittivity calculation of a single-component dielectric material ($d > 95\ \%\ d_{th}$). Also, we tried to apply certain mixing rule relevant for multi-component dielectric material and in the following calculations we consider bulk $SrZrO_3$ relative permittivity 30 and pores filled by air with relative permittivity 1. In the case of multi-component materials, general equation is defined by Lichtenecker logarithmic rule (Eq.2) [15]

$$\log \varepsilon = \sum v_i \log \varepsilon_i \qquad (2)$$

where i is the number of components, v_i and ε_i are the volume fraction and relative permittivity of component i, respectively. In the case of a two-component composite Eq. 3 could be written as

$$\log \varepsilon = v_b \log \varepsilon_b + v_p \log \varepsilon_p \qquad (3)$$

where index b means bulk mass and index p means pores. When immersion-based porosity, i.e. 16 %, is considered, the relative permittivity is 17.4. This value is in accordance with our measured data, Figure 3, particularly in the case of coating sprayed on carbon steel.

Electric DC resistivity, which is an important part of the ceramics behavior in an electric field, is shown in Table 1. The values are interesting to be compared with Yttria stabilized zirconia (YSZ) coatings reported in our earlier work [16]. Relative permittivity is similar to YSZ in the whole frequency range. However, loss factor of $SrZrO_3$ is one order higher and less frequency-stable and in the same time resistivity is two orders of magnitude lower. This is due to high porosity of $SrZrO_3$.

The optical reflectivity versus radiation wavelength is shown in Figure 4. The whole curve is similar to YSZ ceramics, used often in the aerospace industry as TBC.

The band gap E_{bg} of our as-sprayed coating (Table 1) was lower than 5.2 eV reported for $SrZrO_3$ prepared by a polymeric precursor method [17]. Complex oxides containing strontium are often used as optical materials, mainly as luminescent pigments, prepared by various techniques [18]. The substrate type does not influence the electron properties of our plasma sprayed coatings, which manifested itself in the same bandgap value for both types of samples. However, it would influence partly the cohesion of the coatings, c.f. the microhardness results. Because of high thermal expansion of stainless steel in comparison with that of ceramic, the coating should have higher internal stress [19]. The existence of an internal residual stress seems to influence partly the dielectric properties due to microstructure imperfections serving as obstacles for charge accumulation and release. The high loss factor at low frequencies arises from this effect. When the frequency of the AC field becomes higher, the large dipoles stop to be able to participate in the polarization, and only small dipoles on the atomic level act. That are those responsible for the bandgap and this parameter is equal for both sample types. That is why at 1 MHz the loss factor is low and identical for both sample types.

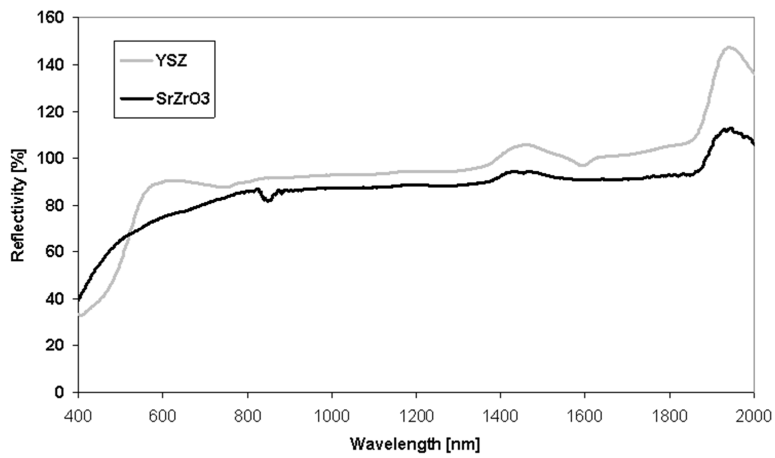

Figure 4: Reflectivity of SrZrO3 coating compared with YSZ coating.

4. Conclusions

Strontium zirconate $SrZrO_3$ was sprayed by a high feed-rate water-stabilized plasma torch WSP at 500A. The torch works at 150 kW and was able to spray $SrZrO_3$ with a spray rate over 10 kg per hour. The as-sprayed coatings exhibited lamellar microstructure and relatively high porosity. This multifunctional material seems to exhibit interesting dielectric performance in the form of plasma sprayed coating. Stainless steel as well as plain carbon steel was used as substrates (preheated over 450 °C) and the coating quality was relatively insensitive to the substrate material.

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