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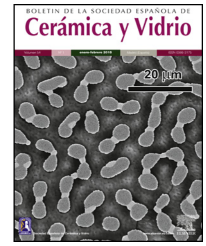

After-glow luminescence of $SrZrO_3$ prepared by plasma spraying

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ABSTRACT

Strontium zirconate $SrZrO_3$ is a multifunctional material studied in literature as a luminescent material, proton-conductor, thermal barrier coating, and dielectric ceramics. In our study this material was sprayed by a high feed-rate water-stabilized plasma torch WSP 500 at its standard electric power 150 kW. The as-deposited coatings exhibited lamellar microstructure with relatively high porosity over 13%. Archimedean (water immersion) specific weight was 4.54 g/cm^3. Annealing was done in air at 1350 °C. Annealed coating exhibited an interesting response to UV light, including after-glow luminescence. After excitation by 225 nm light the sample exhibited after-glow exponential luminescence decay with 5 s characteristic lifetime. Diffused reflectance of the coatings was measured as well. The infrared reflectance is slightly lower after annealing, whereas in the ultraviolet band it is higher.

Luminiscencia posterior al brillo de $SrZrO_3$ preparada por proyección de plasma

Palabras clave:
Proyección por plasma
Zirconato de estroncio
Reflectancia
Luminiscencia

RESUMEN

Un material multifuncional, el zirconato de estroncio ($SrZrO_3$), estudiado en la literatura como material luminiscente, conductor de protones, recubrimiento de barrera térmica y cerámica dieléctrica se proyectó mediante un plasma estabilizado con agua WSP 500 de alta velocidad de alimentación sobre sustratos de acero inoxidable. Se produjeron revestimientos con un espesor de aproximadamente 1,2 mm. El revestimiento recocido exhibió una respuesta interesante a la luz ultravioleta, incluida la luminiscencia después del resplandor. También se midió la reflectancia difusa de los revestimientos. La reflexión infrarroja es ligeramente más baja después del recocido, mientras que en la banda ultravioleta es más alta.

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Introduction

$SrZrO_3$ belongs to the perovskite family with general formula $A^{2+}B^{4+}O_3$. According to classification of perovskites on the basis of the ionic radii of A and B cations, $SrZrO_3$ and its analogue $CaZrO_3$ have orthorhombic structures [1]. At room temperature $SrZrO_3$ was found to crystallize with either pseudocubic or orthorhombic symmetry [2], and exhibit a volume change due to a phase transition from orthorhombic to pseudotetragonal phase at 730 °C [3]. Detailed investigation of phase transformations was done on $SrZrO_3$ produced using metal chelates as starting materials [4]. Strontium zirconate seems to be really multifunctional. $SrZrO_3$ powder was studied as a photocatalysts for hydrogen evolution from water splitting [4]. Doped $SrZrO_3$ single crystal could also work as a proton conductor [5]. Complex oxides containing strontium are often used as optical materials, mainly as luminescent pigments [6]. Recently, polycrystalline ceramics have been developed to the point where they can compete with the performance of single crystals for light emitting applications [7–9].

Only several reports exist about strontium zirconate prepared by plasma spray process. Porosity of $SrZrO_3$ varying from 8% for high torch power to 37% for low torch power as well as deposition efficiency were correlated with torch input power and spray distance in terms of the particle temperature and velocity [10]. Medium-size (10–50 nm) intragranular pores in $SrZrO_3$ coating (studied by small angle neutron scattering, SANS [11]), found in plasma sprayed coatings, annihilated after annealing. The in situ SANS revealed that this process occurs at 1000 °C at a post-deposition thermal exposure. At 900 °C nanopores are created while at 1100 °C the pores begin disappearing again. Different but related materials to $SrZrO_3$, as Dy-doped Yttria-stabilized Zirconia, were applied as phosphorescent coatings produced by plasma spray [12]. $SrZrO_3$ coating behaves similarly to Cerium-doped Yttrium-Aluminum garnet (YAG) coating studied by us earlier [13]. Ability of Neodymum-doped YAG to serve as a luminophore for white light production in solid state light emitters was examined [8]. In the case of YAG spray coating [13], the light conversion efficiency was so far rather low for e.g. scintillator application. This is because of defects, not completely healed by the thermal annealing of plasma sprayed ceramic material. Similar situation is expectable also in the case of $SrZrO_3$.

The aim of our actual paper is to spray strontium zirconate by a high power and high heat flux torch and study the optical character of the coating. This paper presents after-glow luminescence (AGL) experiments unique in case of thermally sprayed $SrZrO_3$.

Experimental

Feedstock and spraying

Plasma spray grade strontium zirconate powder supplied by Cerac Incorporated (Wisconsin, USA) was used as the feedstock. The powder size was from 74 to 150 μm. Plasma spraying was done by the water-stabilized plasma (WSP) torch [14] at 150 kW power (500 A, 300 V). WSP torch has the advantage of combining stabilizing system and cooling system in one. Water is fed into a specially shaped chamber, where it creates a swirl around the walls. Electric arc is burning between the graphite cathode inside the chamber and a rotating anode placed outside the chamber. Feedstock powder is introduced into the plasma jet outside of the torch using two injectors. These injectors can be positioned at various distances from the exit nozzle for different feedstock chemistry and size.

Table 1 – Image analysis results.

Parameter	Porosity (%)	N.V. per mm^2	E.D. (μm)	Circularity	CIR min
As-sprayed	23.8	2355	8.9	0.511	0.035
Annealed	13.3	2136	7.5	0.568	0.058

The feeding distance used was 80 mm and spray distance 350 mm. Compressed air was used as the feeding gas. The substrates were preheated to 460 °C and the spray run started. Next pass was started after cooling to 170 °C. After each pass of the torch the temperature rose to 350 °C and was pushed down to 170 °C by a compressed air flux before the next pass started. Stainless steel coupons were used as substrates. Coatings with thickness about 1.2 mm were produced.

Thermal post-treatment and characterization techniques

Annealing was done without the substrate, removed mechanically by a careful machining. Annealing of the sample used for the luminescence tests was done in air at 1350 °C for 2 h. Because of numerous structural defects inherently present in the plasma sprayed material it was expectable that for luminescent behaviour certain healing of the defects must be reached and the mentioned annealing regime was selected based on differential thermal analysis as a proper one.

Differential thermal analysis (DTA) curves were obtained by simultaneous thermal analyzer (TG-DTA, Bähr, Germany). A heating rate of 10 K/min was applied up to 1400 °C in air atmosphere (flow rate 5 l/h). The weight of the feedstock powder was 45 mg and it was measured in an alumina crucible. The results were corrected by blank subtraction.

Polished cross sections of the coatings were prepared for microscopic analysis. For a better description of pores, image analysis of light micrographs was applied, and additional criteria besides the porosity percentage were introduced, Table 1. N.V. denotes the Number of Voids per unit area of the cross section and E.D. denotes Equivalent Diameter of voids representing their size distribution. Circularity could vary between 1 (belonging to a circle which represents a globular void, i.e. pore) and 0 (i.e. a line representing a flat pore or a crack). All parameters were calculated for 10 images. Resolution of used light microscopy is sufficient to provide quantification of the porosity commonly present in plasma sprayed coatings.

The phase composition was analyzed by X-ray diffraction (XRD) with CuKα radiation. D8 Discover diffractometer (Bruker AXS, Germany) equipped with 1D detector Lynxeye was used in divergent beam geometry. Moreover, the obtained

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