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Calcium titanate ($CaTiO_3$) dielectrics prepared by plasma spray and post-deposition thermal treatment

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ABSTRACT

This paper studies calcium titanate ($CaTiO_3$) dielectrics prepared by plasma spray technology. A water stabilized plasma gun (WSP) as well as a widely used gas stabilized plasma gun (GSP) were employed in this study to deposit three sample sets at different spray conditions. Prepared specimens were annealed in air at atmospheric pressure for 2 h at various temperatures from 530 to 1170 °C. X-ray diffraction (XRD), Raman spectroscopy and porosity measurements were used for sample characterization. Dielectric spectroscopy was applied to obtain relative permittivity, conductivity and loss factor frequency dependence. Band gap energy was estimated from reflectance measurements. The work is focused on the explanation of changes in microstructure and properties of a plasma sprayed deposit after thermal annealing. Obtained results show significant improvement of dielectric properties after thermal annealing.

1. Introduction

Materials with perovskite structure have received a lot of attention in recent years not only for their possible application in solid oxide fuel cells [1,2] but for their technical importance and excellent properties in a number of areas [3,4]. Calcium titanate ($CaTiO_3$) is one alkaline earth titanate like barium titanate ($BaTiO_3$), magnesium titanium oxide ($MgTiO_3$) and strontium titanate ($SrTiO_3$). These titanates have recently attracted attention because some titanates are used as semi-conductive, ferroelectric and photorefractive materials. Dielectrics based on calcium titanate are widely used in different fields of electronics applications [5–7]. For its high relative permittivity and low dielectric losses $CaTiO_3$ is recommended as a prospective ceramic material for high frequency electronics applications. Dielectric ceramics are used for production of a variety of components such as capacitors, oscillators, filters and resonators for microwave systems.

Plasma spray has become a widely accepted method for preparing coatings with different properties especially thermal barrier coatings which are widely used in the aerospace and power industries. However, coatings or self-supported parts have a variety of other industrial applications including those in electrical engineering. $BaTiO_3$ coatings were successfully sprayed employing the HEPJet spray system. Final coating microstructures were dense, with low porosity and high hardness. Results show that defects in $BaTiO_3$ coatings prepared by supersonic plasma spray reduce the piezoelectric effect [8]. Dielectric properties of plasma sprayed $BaTiO_3$ were investigated as well [9]. High relative permittivity and high loss factor were observed. For this study calcium titanate ($CaTiO_3$), with a tabulated relative permittivity value of 160–170 was chosen to be representative of the low-loss dielectric materials group. Previous studies on properties of plasma sprayed calcium titanate have been completed [10]. Thermal properties of plasma sprayed $CaTiO_3$ and mixtures of $MgTiO_3$–$CaTiO_3$ were studied with results indicating that the thermal diffusivity of both materials decrease with increasing temperature [11]. Thermal post treatment plays an important role in modification of materials properties. This work is focused on explanation of changes in microstructure and properties of plasma sprayed deposits after thermal annealing using several analytical methods described below.

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2. Experimental

2.1. Sample preparation

Industrial purity calcium titanate ($CaTiO_3$) sintered tablets were used. Rietveld analysis of XRD patterns showed a 98.72% content of orthorhombic perovskite phase and 1.28% of rutile TiO_2. Tablets were produced by reactive sintering of calcium carbonate ($CaCO_3$) and titanium dioxide (TiO_2) micro-powders. The final $CaTiO_3$ powder was produced by mechanical crushing and sieving of the sintered tablets to ensure a particle size suitable for spraying (63–125 μm).

Three sample sets were deposited for study in this experiment. Two were produced using a high feed rate water stabilized plasma spray system WSP (WSP 500, IPP ASCR, Prague, Czech Republic) [12]. The distance between the plasma nozzle and substrate, or spray distance (SD), was set to 350 mm and 450 mm for each spray run. Samples were labeled WSP 350 and WSP 450. Spray distance is one of the main parameters in the spray process. At short spray distances the substrate can overheat and affect the coating. In the case of long spray distances, the propelled particles experience cooling and this affects coating deposition. The gas stabilized plasma gun (GSP) operates at a lower temperature and plasma enthalpy compared to the water stabilized plasma gun (WSP). Due to this fact, spray distance is shorter than for WSP. In the current experiment, powder feed-rate was between 22 and 24 kg/h for WSP deposition. A conventionally used atmospheric plasma spray (APS) system equipped with a gas-stabilized plasma gun, F4 [13], was used for spraying the third set of samples. This sample set was sprayed at a standoff of 100 mm and labeled GSP 100. Powder feed-rate was between 2 and 4 kg/h for GSP 100 samples. Substrate was preheated to 150 °C before spraying for all deposits. Spray parameters for both methods are summarized in Table 1.

Coatings were stripped from the substrates by thermal cycling between approximately +150 °C and −70 °C. All samples were annealed in air at atmospheric pressure for 2 h at various temperatures ranging from 530 to 1170 °C to study the induced effects of variable annealing temperatures. The temperature range was chosen with respect to aim of this work, to study annealing effect below $CaTiO_3$ sintering temperature, approximately 1200–1300 °C [12]. Annealing time was selected according to the previous results concerning annealing effect on plasma sprayed deposits [14,15]. A programmable furnace was employed for the experiment and three samples, one from each spray run, were simultaneously annealed during each heat cycle. A typical temperature step was 80 °C with heating and cooling ramps of 7 °C/min for all temperature ranges.

2.2. Characterization

After grinding, in a reduced pressure environment aluminum electrodes were sputtered to surfaces of plan-parallel samples (sample dimensions of approximately 10 × 10 × 1.5 mm). Capacity was measured in a frequency range of 30 Hz–30 MHz. For low frequency measurements (30Hz–100 kHz) a Hioki 3522-50 LCR HiTester was used. The device was set to take the average of four capacity values. Agilent 4285 with a sample fixture Agilent 16451B employs frequency range measurements from 75 kHz to 30 MHz. The frequency step was progressively increased and an applied AC voltage of 1 V was kept constant in both devices. A three electrode measuring system was utilized because this system improves measurement accuracy due to minimizing of the surface currents effect. The electric field was applied along the spray direction (i.e., perpendicular to the substrate surface). Relative permittivity, ε_r, was calculated from measured capacities and specimen dimensions. Simultaneously LCR-meters were used for loss factor measurements. Loss factor, $tg\ \delta$, was measured for the same frequencies as capacity and electrical conductivity was calculated from measured values.

All annealed samples were analyzed by X-ray diffraction. Measurements were performed on a D8 Discover Bruker diffractometer using filtered CuKα radiation and a 1D LynxEye detector. Diffraction profiles were analyzed within the frame of the Rietveld method in TOPAS 4.2 software.

Diffuse reflectance was measured by UV–vis–NIR scanning spectrophotometer (Shimadzu, Japan) with a multi-purpose large sample compartment and corresponding band gap energy was estimated. The reflectance curves obtained between 200 and 2000 nm were converted to absorbance and recalculated [16] to band gap energy, E_{bg}.

Microstructure of $CaTiO_3$ powder was observed using EVO MA 15 scanning electron microscope (Carl Zeiss SMT, Germany). Porosity was studied on polished cross-sections by light microscopy. Ten images of each sample were taken from randomly selected areas at a magnification of 250 times. Evaluation of porosity parameters was completed using image analysis software Lucia G (Laboratory Imaging, Prague, Czech Republic). Only pores larger than 3 μm in diameter were accounted for in the porosity measurements.

Raman spectra were acquired using a DXR Raman microscope by Thermo Scientific Nicolet (USA) using a green laser (532 nm) and power of 3 mW under an objective of 10 magnification with a scanning time of 16 s (8 two-second scans). For calibration samples, mixtures were prepared from pure $CaTiO_3$ and pure

Table 1
Plasma spray parameters.

Parameter	WSP	GSP
Power (kW)	154	24
Primary gas (slpm)	–	Ar; 65
Secondary gas (slpm)	–	H_2; 2.5
Powder feeding medium	Air	Ar
Spray distance (mm)	350; 450	100

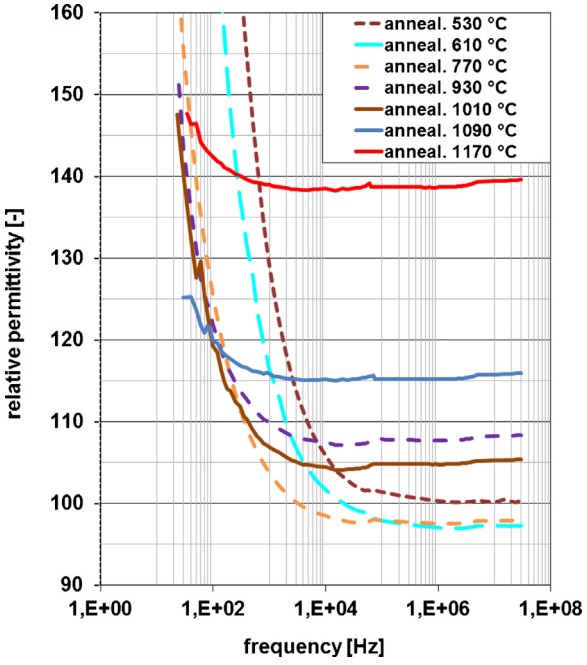

Fig. 1. Frequency dependence of relative permittivity for annealed WSP 450 samples.