PLASMA SPRAYING AND DIELECTRIC CHARACTERIZATION OF ZIRCONIUM SILICATE

PLAZMOVÉ NÁSTŘIKY KŘEMIČITANU ZIRKONIČITÉHO A JEJICH DIELEKTRICKÁ CHARAKTERIZACE

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Abstract

The article is concerned with selected dielectric properties of zirconium silicate $ZrSiO_4$ was plasma sprayed by the water-stabilized plasma system ($WSP^{®}$). The deposits - planparallel plates with a smooth surface - were tested in the alternative low voltage electric field to measure capacity and loss factor in the frequency range from 300 Hz to 1 MHz. Relative permittivity was calculated from the measured capacity. Dielectric strength of $ZrSiO_4$ was measured in DC regime. The results reveal that also after heating almost to 1000°C the difference between samples, caused by various plasma setup parameters, will manifest itself.

Článek se zabývá vybranými elektrickými vlastnostmi zirkonsilikátu $ZrSiO_4$ ve formě plazmových nástřiků připravených vodou stabilizovaným plazmatronem ($WSP^{®}$). Tyto nástřiky – planparalelní destičky s rovným povrchem – byly zkoušeny ve střídavém elektrickém poli nízké intenzity za účelem stanovení kapacity a ztrátového činitele v oboru frekvencí od 300 Hz do 1 MHz. Relativní permitivita byla vypočtena z naměřené kapacity. Elektrická pevnost $ZrSiO_4$ byla měřena ve stejnosměrném poli. Výsledky ukazují, že i po ohřevu k teplotě 1000°C zůstávají zachovány rozdíly mezi vzorky, jež byly vneseny odlišnostmi v nastavení parametrů plazmového stříkání.

Key words

plasma spraying, Electrical properties, Zircon, Silicates, Insulators

plazmové nástřiky, elektrické vlastnosti, zirkonsilikát, silikáty, izolanty

Introduction

Zircon, zirconium silicate $ZrSiO_4$ is a natural mineral used various applications as a refractory bulk material. It is an excellent feedstock for the plasma spraying of protective coatings and free-standing bodies. Zircon decomposes on spraying (at temperatures above 1676°C) into tetragonal ZrO_2 and amorphous SiO_2, which can be preserved in deposits by fast cooling. This combination of zirconia and silica exhibits properties such as high thermal shock resistance, good corrosion resistance, low wettability, etc. Zircon is one of the technologically important oxide ceramic materials known for its refractoriness, its low thermal expansion and low thermal conductivity.

Zirconium silicate is found in nature associated with acidic igneous rocks, from which zircon sand form through weathering. After additional treatment, in which small amounts of impurities like rutile are separated, zircon sand is used as a refractory material for glazes, enamels, and as a row material for electrotechnical ceramics. The nominal composition of that product is 67 wt% of ZrO_2 and 33 wt% SiO_2, but usually there are small amounts of Fe_2O_3, cerium, thorium, or hafnium.

The thermal dissociation of purified and unpurified bulk zircon refractory was studied in **[1]** by ambient- and high-temperature X-ray diffraction to understand the high-temperature performance of brick made from this material. Most of the data were collected on powders at or below 1650°C; however, data were collected between 1400° and 2000°C. In addition, small pieces of the refractory were heated to 1650°C, cooled to room temperature, and then examined under ambient conditions. The degree of dissociation was shown to be dependent on purity, particle size, peak temperature, and time at temperature. High-temperature mass spectrometry showed that the silica is vaporized at elevated temperatures.

Zircon is one of the most commonly used feedstock for plasma spraying with water-stabilized plasma (WSP) system **[2]**. Zircon is usually not very sensitive on spray parameters and a wide variety of setup specifications could be used for manufacturing of coatings with similar properties. Although SiO_2 has lowest critical undercooling parameter, the large difference in melting points between silica and zirconia results in metastable zirconia appearing from the melt first instead of from the silica. The cooling rate determines if tetragonal or cubic zirconia will form in the sprayed material.

Naturally occurring zircon sand was plasma spray coated **[3]** on steel substrates previously coated with NiCrAlY bond coat. The coatings were characterized for their microstructure, chemical composition, thermal shock resistance, and the nature of structural phases present. The as-sprayed coatings consisted of t-ZrO_2 (major phase), m-ZrO_2, $ZrSiO_4$ (minor phases), and amorphous SiO_2. These coatings, when annealed at 1200°C/2 h yielded a $ZrSiO_4$ phase as a result of the reaction between ZrO_2 and SiO_2.

Plasma spraying of Al_2O_3/$ZrSiO_4$ was performed **[4]** using spray dried and plasma spheroidized powder feedstock. The mixtures were sprayed using different spray stand-off distances and plasma power levels. X-Ray diffraction was used to characterize the phase composition and scanning electron microscopy examined the morphology of the sprayed surface and polished cross-sections. The results showed that the plasma spray process parameters played an important role in the final outcome of microstructures of the coatings. The coatings produced with spheroidized powders displayed a much denser structure than those produced with the spray-dried powders. The phase composition analysis showed the presence of amorphous phases in addition to crystalline alumina, zircon and tetragonal (t) zirconia (ZrO_2). Transmission electron microscopy showed that amorphous phases and t-

ZrO_2 crystals with particle size 100–200 nm could coexist within a single splat due to the relatively low local cooling rate.

Self-supported $ZrSiO_4$ coatings have been deposited by means of atmospheric pressure plasma spraying, a high rate deposition method. However, it is well known that $ZrSiO_4$ dissociates into ZrO_2 and SiO_2 in the high temperature plasma torch during plasma spraying, the rapid quenching preventing reverse combination of both components into $ZrSiO_4$. Usually, high temperature annealing (about 1500 °C) is applied in order to combine SiO_2 and ZrO_2 into $ZrSiO_4$. In **[5]** an attractive technological alternative was investigated to recombine SiO_2 and ZrO_2 into $ZrSiO_4$ by laser treatment with a scanning continuous wave CO_2 laser. The addition of SiO_2 rich glassy particles to the plasma spray powders was realized in order to facilitate the recombination of ZrO_2 and SiO_2 into $ZrSiO_4$ during laser treatment. After carefull adjusting the CO_2 laser treatment parameters (laser power density, scanning speed) the SiO_2 and ZrO_2 phases indeed recombined into $ZrSiO_4$. It appeared that the addition of low melting point SiO_2 rich particles strongly enhances the reaction of zirconia and silica into zircon.

Effects of spray parameters, such as spray distance, SD, and substrate temperature, T_S, and post heat treatment on the structure and properties of plasma-sprayed zircon coatings were investigated in **[6]**. Zircon was totally decomposed by plasma spray; the coatings were composed of tetragonal zirconia (t-ZrO_2) and amorphous silica (a-SiO_2), because of the rapid cooling of molten particle right after the impingement to the substrate. Porosity of the as-sprayed coatings was highly affected by both of substrate temperature and spray distance. In all range of the spray distance which had been tested in this study, higher substrate temperature resulted in lower porosity of the coatings; the coating with porosity of 2 % was obtained at T_S=1300°C with SD=95mm. Porosity also decreased with decrease of spray distance. By the heat treatment at 1200°C, t-ZrO_2 transformed to monoclinic zirconia (m-ZrO_2) and a-SiO_2 crystallized to cristobalite, respectively. Cracks in the coating disappeared, and open porosity decreased. This can be attributed to sintering of SiO_2 and phase transformation of ZrO_2. After the heat treatment at 1400°C, the coating was composed of $ZrSiO_4$ with dispersed fine m-ZrO_2 particle. Open porosity of all the coatings increased up to 10% at this temperature. This is because of volume shrinkage during the formation of zircon.

The high Ts coating also indicated high adhesive strength to graphite substrate **[7].** Even after the heat treatment at 1200°C, open porosity of high Ts coatings was maintained as low as 2%, while that of low Ts coatings was high.

Electrical characterization of WSP sprayed zircon was never reported before. The subject of our paper is to report a measurement of dielectric permittivity and loss factor of plasma sprayed zircon after a special type of heat after-treatment. Other, but more complex and here only partly presented task was to find spray setup parameters prospective for the production of low-loss and stable-permittivity material.

Experimental

Zircon powder was plasma sprayed with water-stabilized plasma (WSP) system. The spray process was carried out to enable obtaining of self-supported parts, similar to those referred in **[5].** Variety of spray distances SD was applied to test its importance, similarly to **[6]**.

The heat after-treatment treatment consists of heating onto 960°C and subsequent cooling practically without delay on the temperature. The motivation of this treatment was to promote crystallization of the amorphous silica in the structure, but suppress a pronounced grain growth of the new crystalline phase.

Free-standing bodies were made with a wall thickness of 1 to 2 millimeters. Electric measurements were carried out **[8]** at the CTU in Prague, Faculty of Electrical Engineering, Dept. of Mechanics and Materials Science, Czech Rep. The electric field was applied parallel to the spraying direction (i. e. perpendicular to the substrate surface). Capacity was measured in the frequency range from 300 Hz to 1 MHz using programmable LCR-meter (PM 6306, Fluke, USA). The frequency step was exponential on the entire studied range. Test signal voltage was 1V AC, the stabilized electric LCR-meter was equipped with a micrometric capacitor as recommended in the relevant standard **[9]**. Relative permittivity ε_r was calculated from measured capacities and specimen dimensions. This same LCR-meter (PM 6306) was used for the loss factor measurement. Loss factor tg δ was recorded at the same frequencies as capacity. Five specimens of each production parameters were tested and averages calculated. Precision of the measurement is ± 10 percent.

Breakdown voltage was measured on the in-house made apparatus **[8]** (Dept. of Electrotechnology, Faculty of Electrical Engineering CTU, Prague) convenienced to the relevant standard **[10]**. Samples were tested without sputtered electrically conductive contacts to prevent flashover reported earlier for similar silicate coatings **[8]**. Continuous increase of the applied voltage in DC regime (ambient atmosphere, room temperature) was maintained until breakdown or flashover occurs. Dielectric strength was calculated from breakdown voltage and specimen thickness. Six specimens of each production parameters were tested.

Results and discussion

The microimage of polished cross section prepared from as-sprayed zircon is given on the Fig. 1. The main defects inherently present are visible: porosity (black), unmelted particle (circular with circular pores inside) and inter-splat boundaries with dominant horizontal orientation – perpendicular to spray direction. Those entire features have certain influence on coating behavior including dielectric properties.

Figure 2 displays the results. On the left part the dependence of relative permittivity on the frequency of the field is shown and on the right part the same dependence of the loss factor. Thee different setup parameters are displayed. The value permittivity is similar to that for zircon as-sprayed coating (ε_r = 10.4, measured only at 1 kHz), the permittivity of all samples is stable in the whole frequency range. The loss factor of annealed plasma deposits exhibits certain decrease with increasing frequency up to approx. 50 kHz and certain growth with further frequency increase. The values are in general in the frames from 0.01 to 0.1, which is slightly higher than that for zircon as-sprayed coating (tg δ = 0.0082, measured only at 1 kHz). The sample 23-200 is the worst – lowest permittivity and highest losses, which is probably due to overheating at spraying (FD – e.g. 23 and SD – e.g. 200 indicates the feeding and spray distances in [mm], respectively **[11]**). Combination of the shortest FD (very high temperature at feeding point) and shortest SD (very high temperature at impact point) leads to rather metastable structure.

Electric strength of $ZrSiO_4$ as-sprayed coatings is shown on the Fig. 3 as a function of spray distance for two feeding distances. The values are between 4 and 7 kV/mm and the best result is obtained on SD=350mm. This result confirms the fact that optimal spray distance for WSP spraying of silicates is 300 mm and larger **[8].** The spray process itself seems to be responsible for the difference between samples; the influence of annealing is negligible.

Influence of FD on breakdown voltage is following: Shorter FD means higher melting degree, so the interlamellar contact is better and structural imperfections providing a path for the breakdown streamer are limited.

Rapid melting of the ceramic body occurs directly before breakdown. Here the resistance locally decreases and enables cumulating of the charge until short-circuit is completed through the specimen thickness. At the short-circuit, current of 20 - 30 mA flows through the specimen.

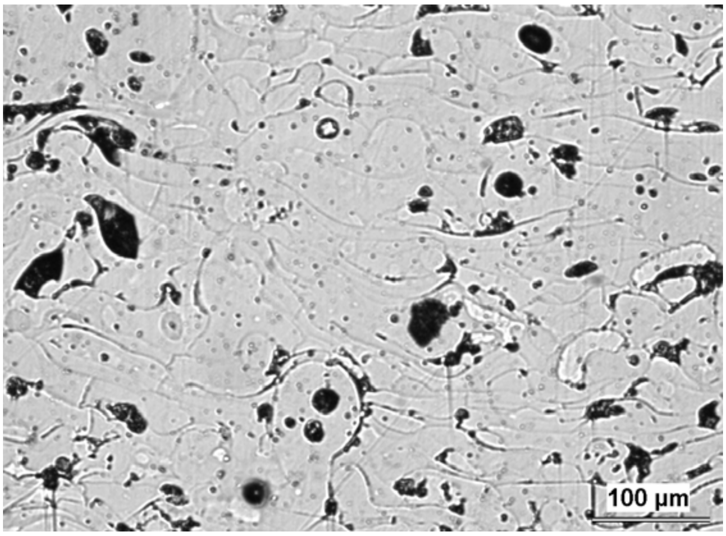

Fig. 1. *Cross section of $ZrSiO_4$ coating produced by WSP spraying*

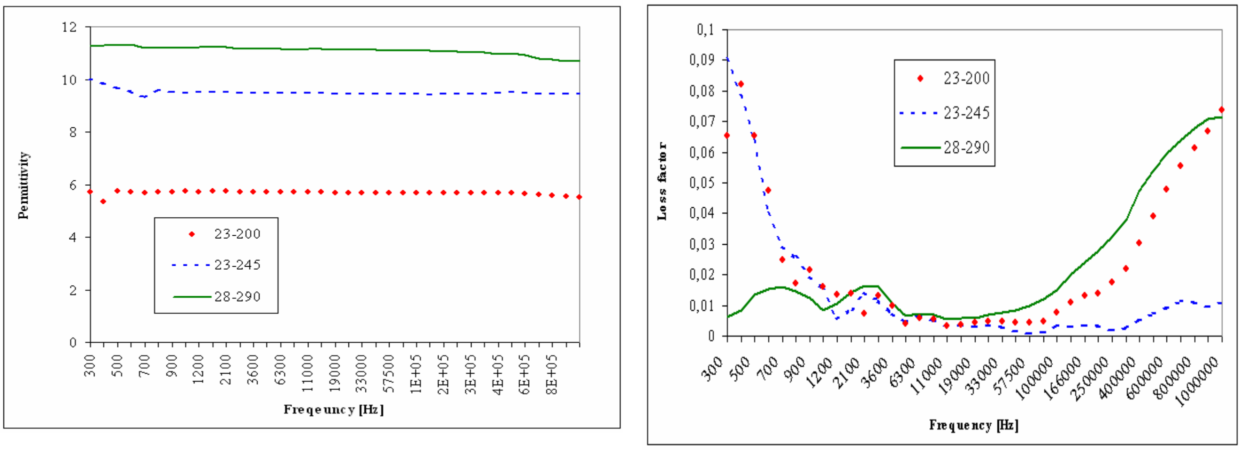

Fig. 2. *Permittivity and loss factor of $ZrSiO_4$ annealed coatings*

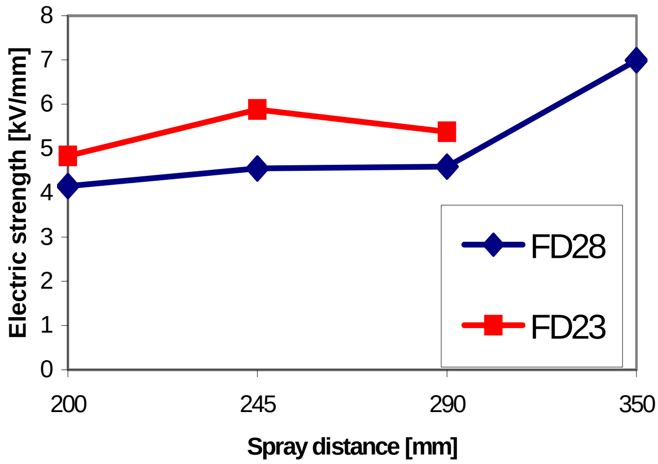

Fig. 3. *Electric strength of $ZrSiO_4$ as-sprayed coatings*

Conclusions

Zirconium silicate was plasma sprayed and annealed at temperature lower than is reported temperature range responsible for dramatic phase, structural and volumetric changes.
Selected dielectric properties were studied on as-sprayed and also annealed coatings. The results reveal that also after heating almost to 1000°C the difference between samples, done by various plasma setup parameters, will manifest itself.

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