

Influence of chemical composition on dielectric properties of Al_2O_3 and ZrO_2 plasma deposits

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Abstract

Aluminum oxide, zirconium oxide and their mixture were plasma sprayed by a water-stabilized plasma gun. Resulting deposits were studied as dielectrics. Capacity and loss factor were measured for the frequency range 200–10⁶ Hz and relative permittivity was calculated. Electric resistance was also measured and volume resistivity calculated for all studied materials. It was proved that dielectric behavior of plasma sprayed oxide ceramics like alumina- and zirconia-based materials at low voltage follows the expectations based on the knowledge of dielectric behavior of sintered ceramics.

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1. Introduction

Aluminum oxide and zirconium oxide are two important ceramic materials very widely utilized in plasma spray processes to produce parts of machines for numerous industrial applications. Aluminum oxide (Al_2O_3) has a rather complicated phase structure, which has been described fully in many studies, such as [1,2]. The most important phases are α (corundum) and γ . Zirconium oxide (ZrO_2) is widely studied especially after the discovery of transformation toughening. There exist many papers dealing with the structure and properties of this material, for example Refs. [3–5]. Monoclinic, tetragonal and cubic phases exist subsequently with increased temperature.

Before successfully applying these materials in plasma spraying it was necessary to resolve the problem of how to stabilize the desirable phases in the deposits. In the case of ZrO_2 , the approach to the stabilization in thermal spraying is the same as in the general stabilization of the cubic phase at room temperature—the feedstock powder is the solid solution of ZrO_2 with a stabilizer

such as Y_2O_3 (the resulting material is often labelled YSZ), CaO (CSZ) or MgO (MSZ) [6]. For Al_2O_3 it was necessary to find a proper stabilizer and its concentration if the dominant content of the α phase in the deposit is desirable. Chromium oxide Cr_2O_3 that creates a solid solution with Al_2O_3 was found as a proper stabilizer to ensure it [7]. If a mixture of α and γ phases is allowed in the deposit, pure Al_2O_3 (‘white alumina’) or mixture Al_2O_3 with approximately 3% TiO_2 and 1% Fe_2O_3 (‘gray alumina’) is sprayed.

Zirconium oxide is an excellent thermal insulator among ceramic materials. Moreover this property is rapidly enhanced by plasma spraying thanks to the unique lamellar microstructure of the deposit. Plasma sprayed zirconia as well as alumina and also some other ceramics are in the state of plasma sprayed coating used as ‘thermal barrier coatings’ [8].

If electric industry applications should be listed, first of all it must be pointed out that YSZ is an important ionic conductor widely utilized as a solid electrolyte [9]. Based on this type of electrolyte, active at high temperatures and for oxygen ions only, are solid oxide fuel cells (SOFC). This application for some 10 years has been a serious challenge for plasma spraying because of the necessity to create a multilayer composition of different materials. The complexity of the topic is with the

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accent on YSZ, most comprehensively described in [4,10]. From the point of view of plasma spraying the most promising approaches are referred to in [11–14].

Aluminum oxide and zirconium oxide are probably the most widely utilized materials in thermal spraying, therefore some basic studies, prospectively helpful to understand coating behavior in general, were carried out on these materials, for example Refs. [15–17].

From the point of view of dielectric properties there is a lack of comprehensive studies of plasma deposits from these materials. Important results have been created by Pawlowski [18]. This study summarizes relative permittivity, loss factor and electric strength measurement results on Al_2O_3 deposits manufactured from feedstock powders with different size and chemical purity. Frequency dependence is included only for permittivity and in a narrower frequency range than in our case. In recent times studies have been carried out at elevated temperatures only [19,20] to prove the deposits' insulating ability if it should apply as an insulating part of SOFC [19] or in fusion reactors [20].

2. Experiment

2.1. Material selection

The authors' approach utilizes experiences gained on titanates and silicates [21–25]. In their opinion no materials exist which are absolutely suitable for a comprehensive study of the behavior of plasma sprayed ceramics in general in the electric field. Some titanates exhibit excellent chemical and phase stability during spraying [21], but a strong relaxation of permittivity was observed, which, on the other hand, is not typical for example for silicates. Anomalies in silicates are caused by their amorphous character in an as-sprayed state [25]. Alumina has a rather complicated phase structure and moreover a very small loss factor, which are disadvantages of this material for such a purpose. Stabilized ZrO_2 seems to be slightly better—it exhibits higher relative permittivity in a sintered state.

The authors decided to measure alumina- and zirconia-based deposits frequently used in the plasma spray research and also one mixed material composed from Al_2O_3 and ZrO_2 (see Table 1). Despite this type of

composition is well known in technical practice (e.g. 'zirconia toughened alumina' [26]), no dielectric characterization of such plasma deposit has been reported.

2.2. Plasma spraying

The samples were manufactured using a high-throughput water-stabilized plasma spray system, WSP[®] PAL 160 (Institute of Plasma Physics, Prague, Czech Republic). This system operates at about 160 kW arc power and can process substantial amounts of material per hour. Main spray parameters of this system—feeding distance and spray distance—were optimized by testing single splat shapes and sizes as well as powder spheroidization in plasma before deposition of the samples. Optimum preheating temperature of the substrate (300 °C) was also found by single splat testing.

As substrates, flat carbon steel as well as stainless steel coupons were used. Substrate roughness R_a was 8 ± 1 μm . The powder was forced in by compressed air through two injectors. Deposited thickness was about 1 mm for coatings and 2.5 mm for subsequently stripped deposits. Thick deposits were stripped from the substrate by a releasing agent or by thermal cycling.

2.3. Measurements

2.3.1. Specimen preparation

The surface of the specimens was ground after spraying to eliminate roughness, which is an inherent property of plasma sprayed coatings. There are two types of specimen. The first one is stripped-out from the substrate and ground from both sides to produce plan-parallel plates with a smooth surface. Such specimens are in principle monoblock capacitors with the dimensions $10 \times 10 \times 1$ mm. The second type is a coating on the metallic substrate. In this type only the topside was ground. A thin layer of aluminum as the electrode (at plan-parallel plates from both sides) was sputtered in reduced pressure on the ground surface.

2.3.2. Description of the electric measurements

Electric measurements were carried out in Prague at the Czech Technical University's Faculty of Electrical Engineering, Department of Mechanics and Materials Science in the Czech Republic. 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 200 to 1 MHz using a programmable LCR-meter (PM 6306, Fluke, USA). The frequency step was 100 Hz between 200 and 1000 Hz, 1 kHz between 1 and 10 kHz, 10 kHz between 10 and 100 kHz and 100 kHz between 100 and 1 MHz. The applied voltage was 1 V AC, the stabilized electric source was equipped with a micro-metric capacitor in accordance with the relevant standard

Table 1
Materials selected for experiments

Material (label)	Composition	Feedstock size (μm)
AH	$\alpha\text{-Al}_2\text{O}_3 + 3$ wt.% $\text{TiO}_2 + 1$ wt.% Fe_2O_3	40–50
YSZ	$\text{ZrO}_2 + 8$ wt.% Y_2O_3	40–75
AZ40 ^a	60 wt.% AH + 40 wt.% YSZ	40–63

^a Supplier: Norton (MA, USA).

[27]. Relative permittivity ϵ_r was calculated from measured capacities and specimen dimensions [22].

This same LCR-meter (PM 6306) was used for the loss factor measurement. Loss factor $\text{tg } \delta$ was measured directly at the same frequencies as capacity.

Electric resistance was measured with a special adaptor—model 6105. The electric field was applied by a regulated high-voltage supply and the values read by a multi-purpose electrometer (617C, Keithley Instruments, USA). The applied voltage was 100 ± 2 V DC. A three-electrode configuration was used in this setup to prevent stray pickup and to ensure constant pressure over the measured sample. Volume resistivity was calculated from the measured resistance and specimen dimensions [22]. The values in the chapter ‘results’ are averages from 3 to 6 specimens.

3. Results and discussion

Relative permittivity results are summarized in Fig. 1. It could be seen that alumina exhibits relative permittivity of about 14 at 200 Hz. This value decreased with frequency only very slightly and remains approximately 12 at 1 MHz. Zirconia exhibits relative permittivity of approximately 22 in the whole range of frequencies with only small peaks probably associated with measurement conditions more preferable than with the material. These values are in good agreement with those for sintered materials [28]. The mixture of both materials—AZ40—is a very stable dielectric with relative permittivity of approximately 12 in the whole frequency range without any drop or fluctuations. The majority of literary resources refer to slightly higher permittivity for zirconia (around 27) and slightly lower for alumina

(around 10) as well as for a mixture $-\epsilon_r = 10.6$ for zirconia toughened alumina CoorsTek, as reported in Ref. [29]. This misfit is probably due to the influence of variations in measurement conditions and variations in exact chemical and phase composition of the literature referred to and our samples. It could also be concluded

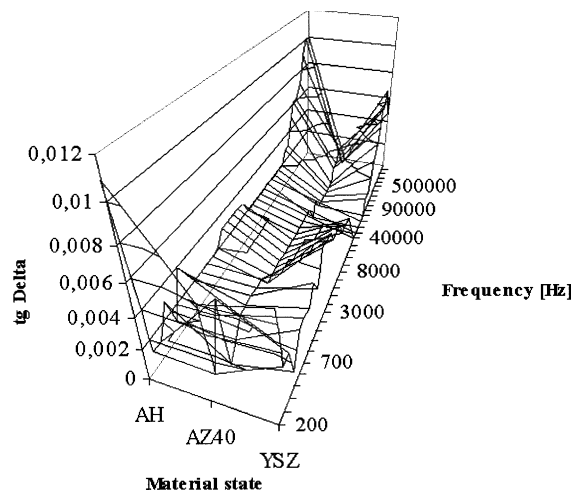


Fig. 2. Loss factor $\text{tg } \delta$ of the deposits. The positions of AH and YSZ are exchanged compared with Fig. 1 for better insight.

Table 2
Volume resistivity Ωm of studied materials

Material	Plasma sprayed	Sintered
AH	3.95×10^9	10^{11} [28]
YSZ	1.7×10^8	10^{11} [28]
AZ40	1.4×10^{10}	10^{12} [29] ^a

^a For ‘zirconia toughened alumina CoorsTek.’

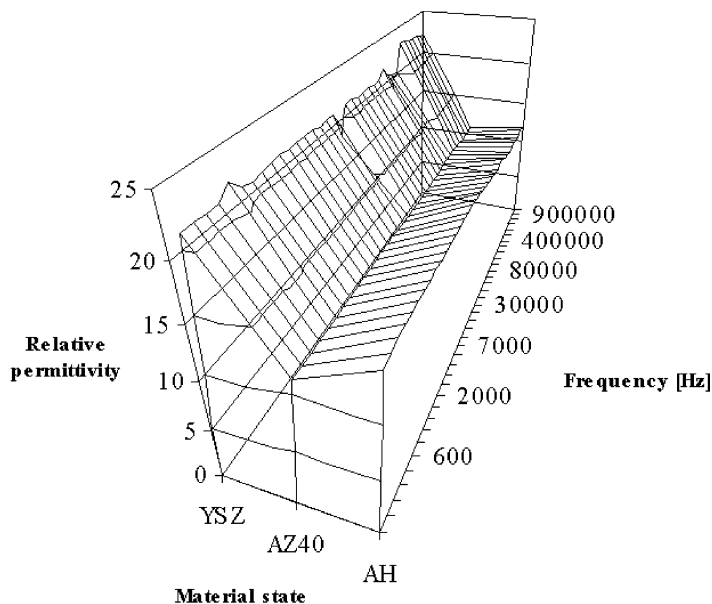


Fig. 1. Relative permittivity of the deposits.

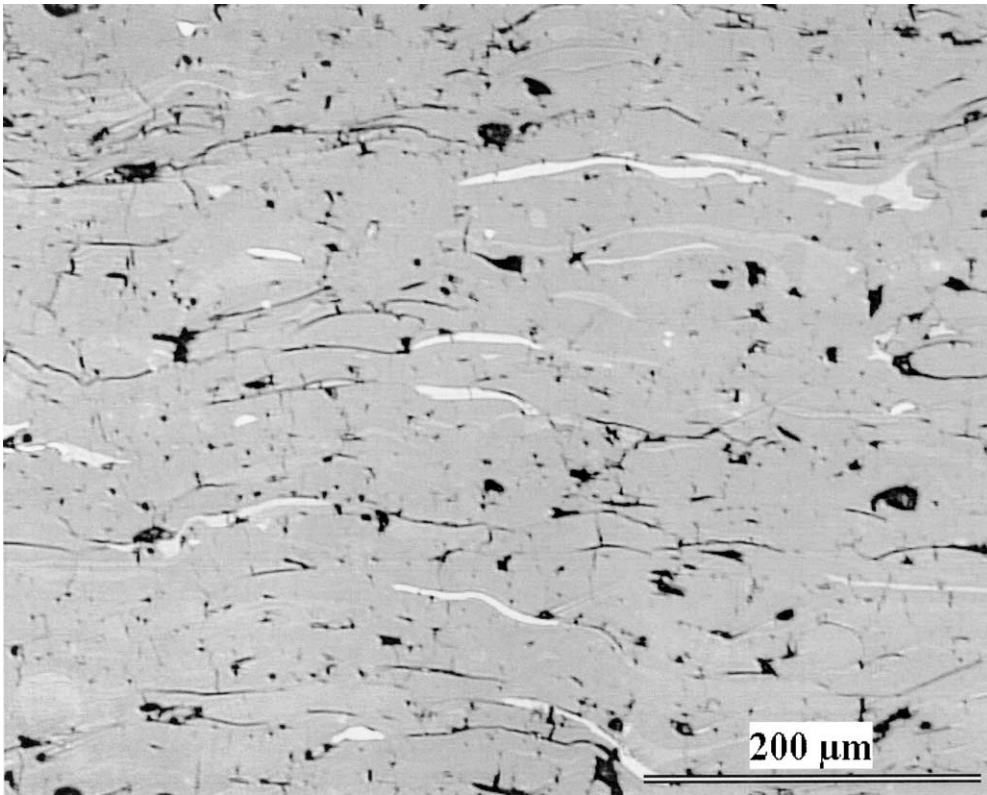


Fig. 3. Microstructure of plasma sprayed alumina, light microscopy.

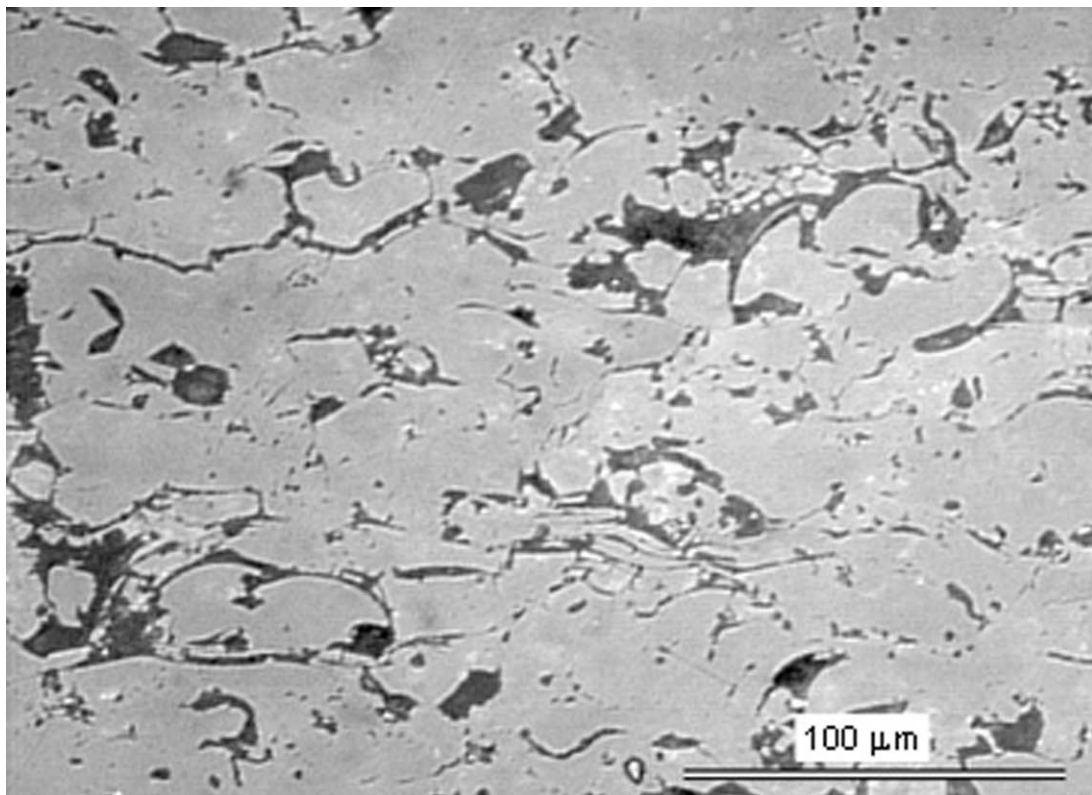


Fig. 4. Microstructure of plasma sprayed zirconia, light microscopy.

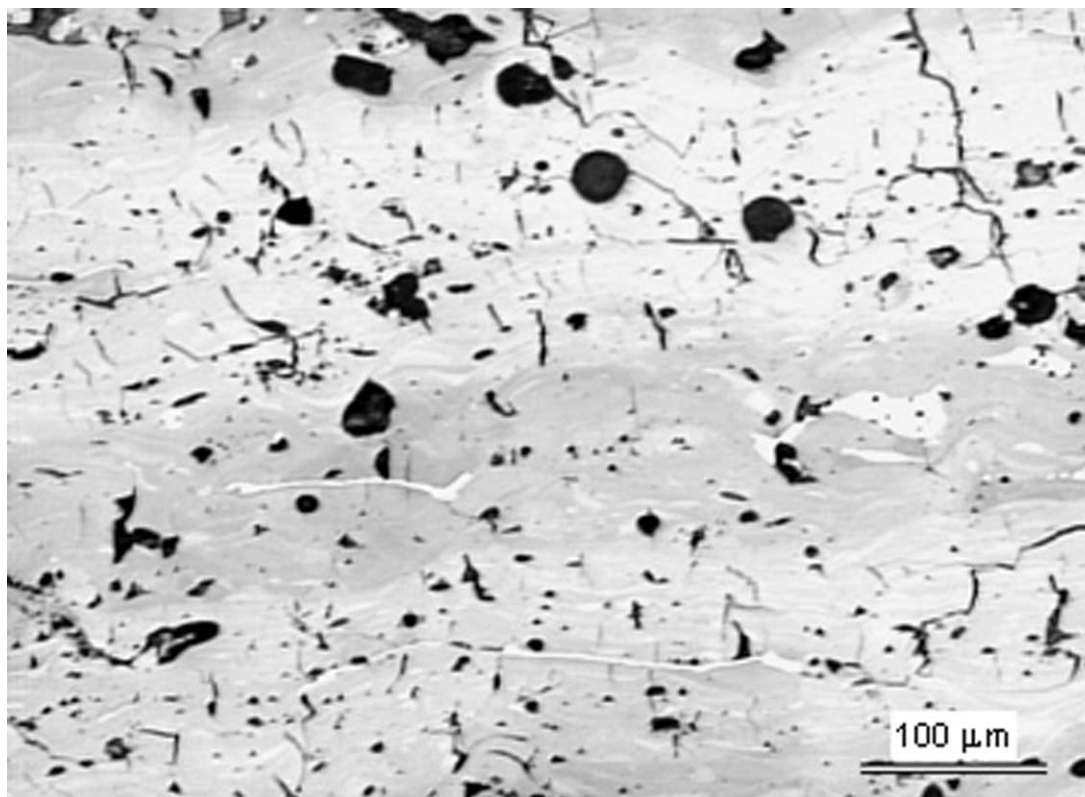


Fig. 5. Microstructure of plasma sprayed AZ40, light microscopy.

that plasma spraying does not cause any changes in the permittivity of studied materials.

Loss factor of the deposits can be seen in Fig. 2. All studied materials exhibit a low loss factor—lower than 0.01—in the whole studied frequency range. In the range from 500 Hz to 500 kHz values are below 0.004, which is the perfect result for plasma deposits. These values are in rather good agreement with sintered materials. With alumina such values are higher compared to sintered alumina (maximum to 5×10^{-4} [27]). But Pawlowski reported 0.02–0.05 at 1 kHz regarding plasma deposited alumina [18] whereas in our study it is 0.002 at 1 kHz. This value is found for α -alumina in [18] and we already have the deposit composed dominantly from this phase. The loss factor of alumina as well as zirconia exhibits stronger increases at higher frequencies than those of AZ40.

Volume resistivity of studied materials was calculated from measured resistance and specimen dimensions [22]. We decided to carry out resistivity measurements to help us resolve them if it is an inherent property of alumina and zirconia deposits to have a frequency-dependent loss factor.

All values for plasma sprayed samples are minimally one order lower than these of sintered ceramics (Table 2). But compared to other plasma deposited ceramic materials [24,25], the alumina–zirconia system

seems to be a relatively good insulator in the as-sprayed state. It is visible that AZ40 having the lowest and only weekly frequency-dependent loss factor have also the highest volume resistivity. Microstructure of all tested materials is documented in Figs. 3–5.

4. Conclusions

4.1. General

‘Gray’ alumina, stabilized zirconia and their mixture AZ40 were plasma sprayed and measured as ‘as-sprayed’ parts without any after-treatment influencing the material structure. The results indicate that plasma spraying does not introduce into those materials any special polarization ability or dielectric response instability as happened with all preliminary studied materials by the authors [22–25]. There is also no serious reason to support the statement [18] that moisture adsorbed within the voids is responsible for differences between the values of plasma deposited and sintered ceramics. Relative permittivity of studied materials is frequency independent. Loss factor of end members slightly grows above 500 kHz and we were not able to come to a decision whether this tendency is more pronounced above 1 MHz or not.

4.2. Suitability for the basic physical study

Resistivity results, in combination with the loss factor and permittivity, show that the conductive part of losses plays a stronger role than the polarizing part. Also these materials—multiphase and without perfect cubic symmetry in the lattice (compared to perovskite titanates [22–24]) and on the other hand without amorphous phase (compared to silicates [25])—seem to be a prospect for dielectric studies of plasma deposits in general. The main disadvantage—if we disregard the phase composition as a non-key factor—remains that the permittivity and loss factor of those materials are very low. For measuring the values well above the accuracy limit of commercial LCR-meters it will be necessary to prepare relatively large-area samples.

4.3. Studied materials and their applicability

If we consider the studied materials as those, which have a central position in plasma spray research and market despite their dielectric properties, we could conclude (as was also referred to earlier, e.g. in Refs. 18 and 19) that they could be successfully used as electric insulation in an as-sprayed state. Moreover this usability is here firstly demonstrated on samples prepared by water-stabilized plasma gun. The mixture AZ40 is a good example of material with a more useful dielectric response than the components themselves. This character as in the present work probably arises from a phase mismatch. The material AZ40, or probably another composition closer to the eutectic one [30], seems to have a promising future for applications in fusion reactors.

Acknowledgements

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