Dielectric Properties of HVOF Sprayed Ceramic Coatings

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Abstract— **Thermally sprayed ceramic coatings can be used as electrical insulators for example in high temperature applications (e.g. fuel cells) or in other demanding conditions. In electrical insulation applications the mostly used coating materials are aluminum oxide, magnesium oxide and magnesium aluminate. In general, only few reports of dielectric properties of thermally sprayed ceramic coatings can be found in literature and further analysis is thus needed. In addition, the measurement methods and conditions in previous research are often not fully documented, complicating the evaluation and comparison of the properties of different coatings. The aim of this paper was to characterize dielectric properties of thermally sprayed ceramic spinel coating sprayed with high-velocity oxygen fuel (HVOF) technique. The studied dielectric properties are DC resistivity, DC dielectric breakdown strength, as well as permittivity and dielectric losses at different frequencies. All measurements were made at temperature of 20 °C and at relative humidity of 20 %. Dielectric properties and the composition of coating material are presented and analyzed.**

Keywords— thermal spraying; HVOF; spinel; coating; resistivity; dielectric spectroscopy; dielectric breakdown strength

I. INTRODUCTION

Thermally sprayed insulating ceramic coatings can be used in demanding conditions where normal insulating materials such as for example polymers cannot be used. As an electrically insulating coating material the most commonly used materials are aluminum oxide (Al_2O_3) and magnesium aluminate ($MgAl_2O_4$). In general, only little research of dielectric properties of thermally sprayed ceramic coatings can be found in literature. In addition, the measurement methods and conditions in previous research are often not fully documented, complicating the evaluation and comparison of the properties of different coatings.

Earlier studies of electrical properties of thermally sprayed coatings are focused on the HVOF (high velocity oxygen fuel) and plasma sprayed alumina coatings [1, 2, 3, 4]. One paper presented DC resistance and DC dielectric breakdown strength of HVOF and plasma sprayed spinel coatings at room temperature conditions and at high humidity levels [3]. Formerly, dielectric spectroscopy studies have been made only for plasma sprayed alumina [1]. The results of the papers [3, 4] indicate that electrical properties of HVOF sprayed alumina and spinel coatings require to be examined more detailed and it has been already seen that especially the microstructure of a coating affects significantly to the electrical properties.

This paper presents the dielectric properties of thermally sprayed magnesium aluminate (spinel) concentrating on the DC resistivity, relative permittivity and dielectric losses as a function of frequency, and DC dielectric strength. All measurements are performed at temperature of 20 °C and relative humidity of 20 %.

II. EXPERIMENTAL

A. Studied Thermally Sprayed Ceramic Coating

The raw materials of the used spinel powder were AlO(OH) (particle size 40 nm and purity 99.99 %) and $Mg(OH)_2$ (particle size 300 – 1800 nm and purity 99.8 %). The proportions of raw materials correspond to a stoichiometric magnesium aluminum spinel ($MgAl_2O_4$). During the sintering process, aluminum hydroxide and magnesium hydroxide formed to $MgAl_2O_4$ –powder. The used spinel powder was experimentally agglomerated by spray drying (Niro p6.3 pilot) and sintered at temperature of 1300 °C. After sintering, the powder particles had very dense microstructure and particle size of the powder was from 6 µm to 21 µm which is very suitable size for HVOF-process.

The $MgAl_2O_4$–powder was deposited on stainless steel substrate (size of 100 mm x 100 mm) by HVOF –process. Number of studied samples was four (A, B, C and D). Table I illustrates the porosity values of the coatings which were measured by optical micrographs and scanning electron microscope (SEM) with two measuring methods: secondary electrons (SE) and back-scattering electrons (BSE). The coating thicknesses of the samples were defined both from cross section figures of two samples deposited at the same time with samples A, B, C and D, and by magnetic measuring device (Elcometer 456C). In the latter case, the thickness result of a sample is an average value of 10 measurements made along the electrode area. The measurement results are presented in Table II. In Fig. 1 the cross-section figures of the studied spinel coating are shown.

Some deviation is noticed in the thickness values because the substrate is not smooth due to the the sandblasting of the substrate before depositing the ceramic coating. In addtion to that, the coating itself has lamellar microstructure causing a sligthly non-smooth surface.

B. Sample Preparation

Dielectric spectroscopy and DC breakdown measurements were made at temperature of 20 °C and relative humidity of

TABLE I. POROSITY OF THE STUDIED THERMALLY SPRAYED COATING.

Porosity [%]		
SEM/SE	*SEM/BSE*	*Optical micrographs*
0.6	1.74	0.25

TABLE II. COATING THICKNESS OF THE STUDIED SAMPLES.

Coating thickness (µm)			Standard deviation (µm)	
Average from cross-section figure	*Average from magnetic measurement for sample A*	*Average from magnetic measurement for sample D*	*Sample A*	*Sample D*
342	362	359	10.0	9.6

20 %, but the DC resistivity measurements were made at temperature of 20 °C and relative humidity of 25 %.These conditions were maintained at the climate room of TUT High voltage laboratory. The samples were preconditioned at 120 °C for two hours and then stabilized at 20 °C and RH 20 % for 12 hours before measurements. Before DC resistivity and relative permittivity –measurements, a round silver electrode was painted on the middle of a coating. The diameter of the electrode was 50 mm. In addition, a shield electrode was painted around the measuring electrode to neglect possible surface currents. From cross section figures it was studied that the used high purity silver paint did not penetrate inside the studied thermally sprayed coating.

C. DC Resistivity

Resistivity measurements were made using Keithley 6517B electrometer and Keihtley Resistivity test fixture 8009. The test voltage was maintained until a stabilized current level (i.e. pure resistive current) was reached. In practice, the tests were performed at test voltages from 10 V to 1000 V and the stabilized DC current was measured 1000 s after voltage application. At higher test voltages (corresponding to field strengths above ohmic region), the DC current did not fully stabilize during the measurement period. In these cases, the resistivity values were also defined according the currents measured 1000 s after voltage application. The volume resistivity of a material was thus defined according to IEC standard 60093 (or ASTM D257-07). [5,6]

D. Dielectric Spectroscopy

Relative permittivity and dielectric losses of the materials were studied with an insulating diagnosis (IDA 200) analyzer
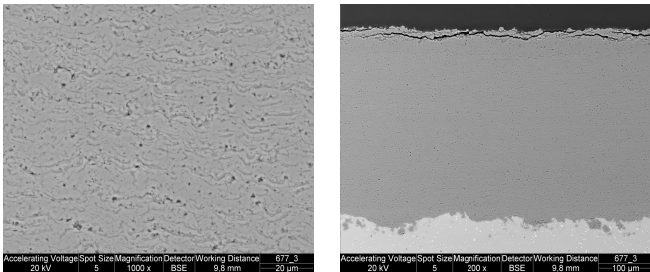

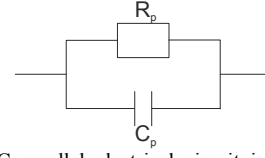Fig. 1. Cross-section figures of the studied coating.

Fig. 2. Equivalent RC parallel electrical circuit in dielectric spectroscopy measurements

device. During the measurements, a sinusoidal voltage with varying frequency was applied over the sample. The true RMS value of the measuring voltage was 140 V. The complex impedance of a sample was calculated from the measured test voltage and the current through a sample which is expressed as the equivalent parallel RC circuit model (Fig. 2). The relative permittivity (ε_r) and dissipation factor (tan δ) were calculated from the measured parallel resistance and capacitance with Eq. (1) - (2):

$$\varepsilon_r \approx \varepsilon_r' = \frac{C_p}{C_0} - \frac{C_e}{C_0}, \tag{1}$$

$$\tan \delta = \frac{1}{R_p C_0 \omega}, \tag{2}$$

where C_p is measured parallel capacitance and R_p parallel resistance of the equivalent circuit model of a dielectric (Fig. 2). C_0 is the so called geometric capacitance of test sample (vacuum in place of the insulation) and ω is angular frequency. The edge field correction (C_e) was not used because the shield electrode was utilized in the measurements. All the test sample arrangements were according to IEC standard 60250 [7].

Loss index (ε_r'') includes all losses of a sample: both conductive and dielectric ones. It can be defined from relative permittivity and dissipation factor, tan δ, with Eq. (3).

$$\varepsilon_r'' = \varepsilon_r \tan \delta \tag{3}$$

E. DC Dielectric Breakdown Strength

Breakdown voltage measurements were made with linearly ramped DC voltage. The measurements were made without immersing the samples into transformer oil because it has been found that the oil immerses into the porous coating and thus increases the dielectric strength of a coating. The used electrode was a flat ended stainless steel rod with a diameter of 10 mm and edge rounding radius of 1 mm. No painted, sputtered or by other means embedded electrodes on the specimen surface were used. The ramp rate of the test voltage was 100 V/s throughout the test until breakdown occurred.

After the breakdown voltage was measured, the thickness of a coating was measured from the breakdown point to define exactly the dielectric breakdown field strength for the coating. The thicknesses were measured with a magnetic measurement device (Elcometer 6517B). Dielectric breakdown field strength of a coating was calculated dividing the breakdown voltage by the corresponding thickness of the breakdown point. The average value of dielectric strength of a sample was calculated from five parallel test results.

III. RESULTS AND DISCUSSION

A. DC Resistivity

Normally the DC resistance of an insulating material is an approximately fixed value (ohmic behavior) at normal service field strengths. During DC resistivity measurements of these samples it was noticed that the conduction of the samples was not ohmic at different voltages. Due to this a more detailed measurement series was performed to find out the region of ohmic conduction and the corresponding change to non-ohmic conduction. Table III presents the resistivity values for samples A and D at different electric fields. Fig. 3 presents the defined resistivity values as a function of electric field. It can be observed that the resistivity of the coating is approximately $3*10^{12}$ Ωm at field strengths below ~0.5 V/μm indicating ohmic conduction behavior but above that a clearly non-ohmic behavior can be noticed. In [8], at high temperatures (800 °C – 1400 °C) it was observed that bulk alumina had ohmic behavior at voltages below 100 V which corresponds approximately field strength of 0.8 V/μm and above 150 V (~1.3 V/μm) it had non ohmic behavior but this was not studied at room temperature conditions [8].

Since the resistivities changed remarkably at higher measuring voltages, some kind of a pre-breakdown behavior may have taken place during the measurements. Due this the measurements were repeated on next day to find out if some permanent changes had taken place during the first measurements. Fig. 4 illustrates the resistivity values of sample A as a function of electric field on the 1st measurement day, when the measurement voltages were from 25 V to 1000 V, and on the 2nd measurement day when the voltages were from 50 V to 1000 V. It can be noticed that material had some

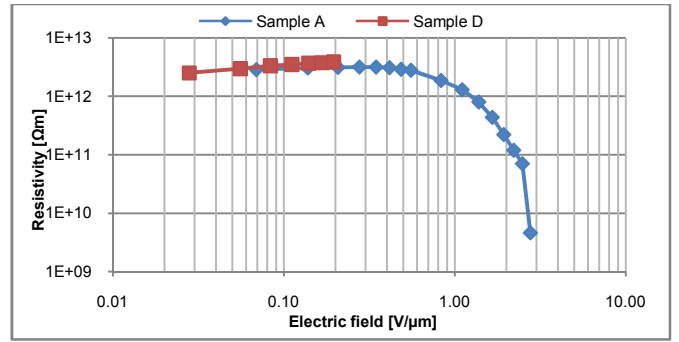
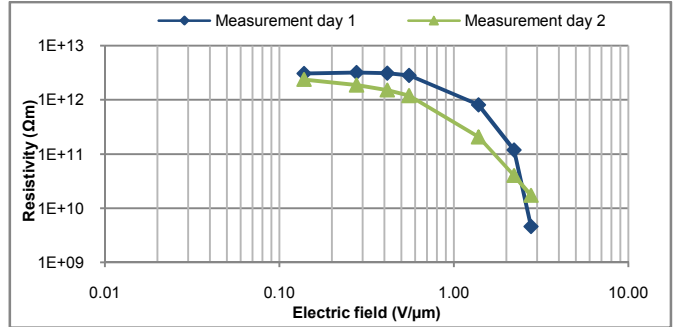Fig. 3. DC resistivity as a function of electric field for samples A.

Fig. 4. Resistivity values of sample A as function of electric field on 1st and 2nd measurement day.

permanent degradation during the first measurements because the resistivity values are lower on the 2nd day than on the 1st day. Some pre-breakdown mechanism probably occurs when the electric field is above approximately 0.5 V/μm.

The observed non-ohmic behavior at relatively low field strengths may be related to the lamellar microstructure of the coating (Fig. 1). The coating consists of areas of bulk spinel material ('splats' formed in the spraying process), very rapidly cooled interfacial layers in between them and air voids which all probably have different dielectric properties. Electric field may thus be inhomogeneous due to this and more highly stressed layers may break down in the pre-breakdown region. The conduction behavior of the coatings will be studied in more detail in the future and for example the role of interfacial areas will be investigated.

B. Dielectric Spectroscopy

Fig. 5 presents the relative permittivity as a function of frequency for the sample A. The relative permittivity is 10.3 at frequency of 50 Hz. In [9], the relative permittivity of bulk

TABLE III. MEASUREMENT VOLTAGE, ELECTRIC FIELD AND RESISTIVITY FOR SAMPLE A AND D.

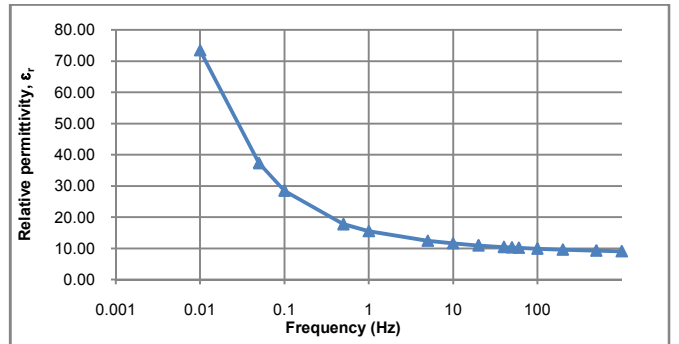| Measurement voltage (V)	Electric field (V/μm)	Resistivity (Ωm) for sample A	Resistivity (Ωm) for sample D
10	0.03		2.54E+12
20	0.06		2.97E+12
25	0.07	2.87E+12	
30	0.08		3.31E+12
40	0.11		3.51E+12
50	0.14	3.05E+12	3.68E+12
60	0.17		3.80E+12
70	0.19		3.87E+12
75	0.21	3.15E+12	
100	0.28	3.18E+12	
125	0.35	3.16E+12	
150	0.41	3.10E+12	
175	0.48	2.92E+12	
200	0.55	2.80E+12	
300	0.83	1.86E+12	
400	1.11	1.29E+12	
500	1.38	8.06E+11	
600	1.66	4.37E+11	
700	1.94	2.22E+11	
800	2.21	1.19E+11	
900	2.49	7.03E+10	
1000	2.77	4.59E+09	

Fig. 5. Relative permittivity of sample A as a function of frequency.

spinel was approximately 8 – 8.5 at 1 MHz [9]. Fig. 6 illustrates the loss index of sample A as a function of frequency. The loss index is 1.1 at 50 Hz. In general, both the permittivity and the loss index are high compared to bulk insulating materials especially at low frequencies. This is probably related to the microstructure of thermally sprayed coatings described in section II. Quite high interfacial polarization may be expected due to the lamellar coating structure increasing both permittivity and losses at lower frequencies. The measuring voltage falls in the ohmic conduction range observed in the DC measurements.

C. DC Dielectric Breakdown Strength

Table IV shows the DC dielectric breakdown strength for samples B and C. Five breakdown results were measured for both samples and average values are defined from these values. The dielectric strengths vary greatly between different measurement points. In [3], the dielectric strength of one type of HVOF spinel ($MgAl_2O_4$) coatings with thickness of 200 μm was ~ 31 V/μm and for a spinel sample of thickness of ~95 μm it was 39 V/μm at room conditions. In [3], it was only indicated that the measurements were made at room conditions and thus the results cannot be directly compared because the humidity affects greatly to the electrical properties of ceramic coatings. The breakdown measurements were performed for as-sprayed coatings without baking samples before measurement and silver painted electrode was used on the top of samples in the breakdown measurements [3]. Because the microstructure, measurement arrangements and measurement conditions are different in this study than in the earlier research [3], the measurement results cannot, anyhow, be directly compared.

IV. CONCLUSIONS

In the DC resistivity measurements, the studied thermally sprayed HVOF spinel coating indicated non-ohmic behavior already at quite low field strengths of approx. 0.5V/μm and above. During DC measurements performed at < 3V/μm field strengths at least some permanent changes were observed. The average DC breakdown field strength of the spinel coating was measured to be 14 and 17 V/μm for the samples, respectively, but the deviation of the results were really high. Relative permittivity and loss index of the material were rather high especially at lower frequencies.
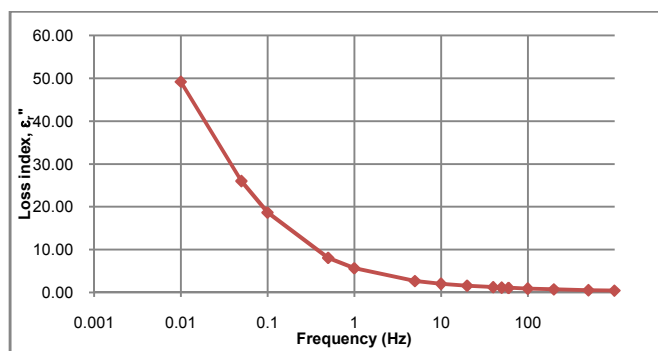

Fig. 6. Loss index of sample A as a function of frequency.

TABLE IV. DC DIELECTRIC BREAKDOWN STRENGTH

Sample	Measurement number	Breakdown voltage (V)	Thickness of the sample (μm) at the measurement point	Breakdown strength (V/μm)	Average breakdown strength (V/μm)	Standard deviation (V/μm)
B	1	3945	342	11.5	13.5	2.1
	2	5680	342	16.6		
	3	4720	347	13.6		
	4	5110	363	14.1		
	5	4065	350	11.6		
C	1	7225	333	21.7	16.9	4.8
	2	4875	348	14.0		
	3	7590	335	22.7		
	4	4190	322	13.0		
	5	4480	338	13.3		

All the results are supposed to be related to the lamellar microstructure (with also some porosity) of thermally sprayed coatings. The probably different dielectric properties of interfacial areas and the bulk may enhance the interfacial polarization and losses especially at lower frequencies. Interfacial layers probably contribute also on the non-ohmic conductivity observed.

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