Influence of Humidity and Temperature on the Dielectric Properties of Thermally Sprayed Ceramic $MgAl_2O_4$ Coatings

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Abstract — **Thermally sprayed ceramic coatings can be used as electrically insulating materials for example in high temperature applications (e.g. fuel cells) or in other demanding conditions where ceramic-based solutions are needed instead of e.g. polymers. The dielectric properties of thermally sprayed ceramic coatings are strongly affected by external conditions. The aim of this paper is to characterize the dielectric properties of thermally sprayed ceramic $MgAl_2O_4$ coatings; especially the effects of ambient conditions on certain dielectric properties of thermally sprayed coatings are studied. DC resistivity at various electric field strengths as well as permittivity and losses at different frequencies is reported in the paper for $MgAl_2O_4$ samples made by three different thermal spray techniques. These measurements were performed at three temperatures as well as at two different relative humidities. The DC breakdown strength was studied at one condition. Due to the slightly open porous microstructure of the studied coatings, increasing humidity particularly increases the dc conductivity and relative permittivity.**

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

I. INTRODUCTION

In high temperature applications (e.g. fuel cells) or in other demanding conditions, ceramic-based insulation solutions are needed instead of polymers. Ceramic material can be thermally sprayed to e.g. demanding geometries. The mostly used insulating coating materials are alumina (Al_2O_3), magnesium oxide (MgO) and magnesium aluminate ($MgAl_2O_4$). Although there are clearly needs and applications for thermally sprayed insulating coatings, in general, only a few studies on the dielectric properties of thermally sprayed ceramic coatings can be found in literature and further analysis is required.

The dielectric properties of thermally sprayed ceramic coatings are strongly affected by ambient conditions [1], [2]. Most of the earlier studies of electrical properties of thermally sprayed coatings are focused on the HVOF (high velocity oxygen fuel) and plasma sprayed alumina coatings [1]–[4]. For $MgAl_2O_4$ (spinel) coatings mainly DC resistivity and DC breakdown strength measurements are performed earlier at room temperature conditions, but in [1] the resistivity was also studied in high humidity [5]. Formerly, dielectric spectroscopy studies have been made for HVOF sprayed alumina at various ambient conditions, but dielectric spectroscopy studies of plasma sprayed alumina as well as HVOF sprayed spinel have been reported only at room temperature conditions [2], [4], [5]. Due to the lamellar and slightly porous microstructure of thermally sprayed ceramic coatings, the influence of temperature and humidity on the dielectric properties is required to be examined in more detail. The aim of this paper is to study the dielectric properties of three differently sprayed spinel coatings at various ambient conditions.

II. EXPERIMENTAL

A. Studied Thermally Sprayed Ceramic Coatings

Three thermally sprayed ceramic coatings of different coating techniques were deposited on stainless steel substrates (size of 100 mm x 100 mm). Experimental $MgAl_2O_4$–powder was deposited by HVOF-process, more detailed information of this HVOF coating is presented in [5]. Commercial $MgAl_2O_4$–powder was deposited by atmospheric plasma spraying and commercial $MgAl_2O_4$ flexicord by flame spraying.

The coating thicknesses of the samples were defined by magnetic measuring device (Elcometer 456B). The mean value of the thickness was calculated from 10 parallel measurements covering the electrode area. The mean thicknesses, standard deviations and gas permeability values of the coatings are presented in Table I. The higher the gas permeability, the more porous the material is. According to the results, the HVOF coating is the least porous and the flame sprayed flexicord is the most porous of the studied materials. Because the coating base is not smooth due to the grit blasting, some deviation is noticed in the thickness values. In addtion to that, the coatings themselves exhibit lamellar microstructure causing a sligthly non-smooth surface. The coatings were tested as-sprayed.

B. Sample Preparation and Test Procedures

DC resistivity and dielectric spectroscopy measurements

TABLE I. THICKNESSES, STANDARD DEVIATIONS AND GAS PERMEABILITIES OF THE STUDIED COATINGS.

Material	Thickness (µm)	SD (µm)	Gas permeability (nm^2)
HVOF	362	10.0	5.85
Plasma	333	10.8	13.1
Flexicord	360	8.1	19.89

were performed at various ambient conditions (+20°C, +40°C, +60°C; RH 20 %, 45 %). The coatings were stabilized at each ambient condition for 3 hours before the measurements. Prior to the stabilizing period at each ambient condition, the samples were dried at 120 °C for one hour and then placed at dry conditions because the same sample was used at all these measurement conditions. At first, the dc resistivity at various electric fields was measured and then the dielectric spectroscopy measurements were performed. In addition, the DC dielectric breakdown strength (DBS) measurements were performed at 20°C, RH 20 %.

For the DC resistivity and relative permittivity measurements, a round silver electrode (∅= 50 mm) was painted on the middle of a coating sample. In addition, a shield electrode was painted around the measuring electrode to neglect possible surface currents. For breakdown measurements, a silver electrode (∅= 11 mm) was painted on the sample surface to improve the contact between the voltage electrode and the coating. Silver paint penetration was studied from cross-sectional optical micrographs. It was observed that the used paint (SPI Conductive Silver Paint) did not penetrate into the coating.

A. DC Resistivity

Resistivity measurements were made using Keithley 6517B electrometer. 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 ranging from 10 V to 1000 V at 20°C, RH 20 % in order to study the resistivity as a function of electric field in detail. At the other ambient conditions, the resistivities were measured at the electric fields of 0.1 V/µm, 0.3 V/µm, 0.5 V/µm, 1.5 V/µm and 2.5 V/µm. The stabilized DC current was measured 300 s after the voltage application. Anyhow, at higher test voltages (corresponding to field strengths above ohmic region), the DC current did not fully stabilize during the measurement period. Despite of this the resistivity values were determined similarly in these cases. All the measuring arrangements were in accordance with the standards IEC 60093 or ASTM D257-07. [5]–[7]

B. Dielectric Spectroscopy

Relative permittivity and dielectric losses of the materials were studied with an insulating diagnosis analyzer device (IDA 200). During the measurements, a sinusoidal voltage with varying frequency was applied over the sample. The measuring electric field was 0.3 V_{peak}/µm unlike in [2], [5] where the measuring voltage was 200 V_{peak} corresponding to the electric fields 0.71 V_{peak}/µm in [2] and 0.55 V_{peak}/µm in [5].

The complex impedance of a sample is calculated from the measured test voltage and the current through a sample which is expressed by IDA device as the equivalent parallel RC circuit model. The relative permittivity (ε_r) and dissipation factor (tan δ) were calculated from the measured parallel resistance and capacitance with Eq.(1)-(2), where C_p is measured parallel capacitance and R_p parallel resistance of the equivalent circuit model of a dielectric. C_0 is the so-called geometric capacitance of test sample (vacuum in place of the insulation) and ω is the angular frequency. The edge field correction (C_e) was not used because the shield electrode was utilized in the measurements. All the test arrangements were performed in accordance with the IEC standard 60250. [8]

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

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

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

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

C. DC Dielectric Breakdown Strength

Breakdown (bd) voltage measurements were made with a linearly ramped DC voltage. The measurements were made without oil immersion because the oil penetrates into the porous coating and thus increases the dielectric strength of a coating. During the breakdown tests, the samples were clamped between two stainless steel electrodes: a rod (∅= 11 mm) and a flat plate (∅=50 mm). The used rod electrode was flat-ended and edge-rounded with a radius of 1 mm. A software controlled linear ramp rate of 100 V/s was used throughout the test until breakdown occurred. [9]

Before painting the silver electrodes on the sample surfaces, the thickness of a coating was measured from the electrode area to define exactly the dielectric breakdown field strength. Dielectric breakdown field strength of a coating was calculated dividing the breakdown voltage by the corresponding thickness of the breakdown point.

D. Statistical Analysis of Breakdown Strength Results

Breakdown process of any dielectric material is inherently of stochastic nature causing statistical distribution of breakdown results. Typically dielectric breakdown strength of solid materials is Weibull distributed due to which also these results were fitted to that distribution. The cumulative density function of a two-parameter Weibull distribution is given in Eq. (4):

$$F(t,\alpha,\beta) = 1 - \exp\left\{ \left(\frac{t}{\alpha} \right)^{\beta} \right\} \tag{4}$$

where *F(t)* is the breakdown probability, *t* is the measured breakdown strength (V/µm), α is the scale parameter (V/µm) and β is the shape parameter (V/µm). The scale parameter represents the breakdown strength at the 63.2 % failure probability and the shape parameter indicates the slope of the theoretical distribution. The statistical analysis was performed using Weibull++ software and the Maximum Likelihood method was used in the parameter estimation.

III. RESULTS AND DISCUSSION

A. DC resistivity

Figure 1 illustrates the resistivities of the coatings as a function of electric field at all studied ambient conditions. The resistivities of all the coatings are at quite a similar level at lowest electric fields at 20°C. When temperature is increased to 40 °C, a permanent change can be seen for the Flexicord coating (which can be seen also in permittivity, Fig. 2). For HVOF and Plasma increasing temperature has not as high influence although DC resistivity of all the coatings decreases when the temperature increases. In general, relative humidity has larger influence on the resistivity in comparison to temperature. The changes, in general, may be linked to the porosity and hydrophilicity of thermally sprayed ceramic coatings.

Flexicord has the highest porosity and its resistivity decreases more with increasing humidity. However, despite the rather high porosity of Plasma coating its behavior does not differ much from HVOF sample. Other properties (e.g. phase composition, interface properties, etc.) are thus also of importance.

B. Dielectric Spectroscopy

The relative permittivities of all the coatings increase especially with relative humidity, as it can be observed from Fig. 2 where the relative permittivity of the coatings is presented as a function of frequency at all the studied ambient conditions. Major permanent changes in the coatings did not occur during the measurements at high temperatures and humidities, except for Flexicord. This is confirmed by the permittivity measurements made after the aforementioned measurements which indicate that the permittivities of the HVOF and plasma samples are only slightly changed in comparison to the initial values at 20°C, RH20%. However, when temperature was increased from 20°C to 40°C, some permanent changes occurred in Flexicord sample which may be

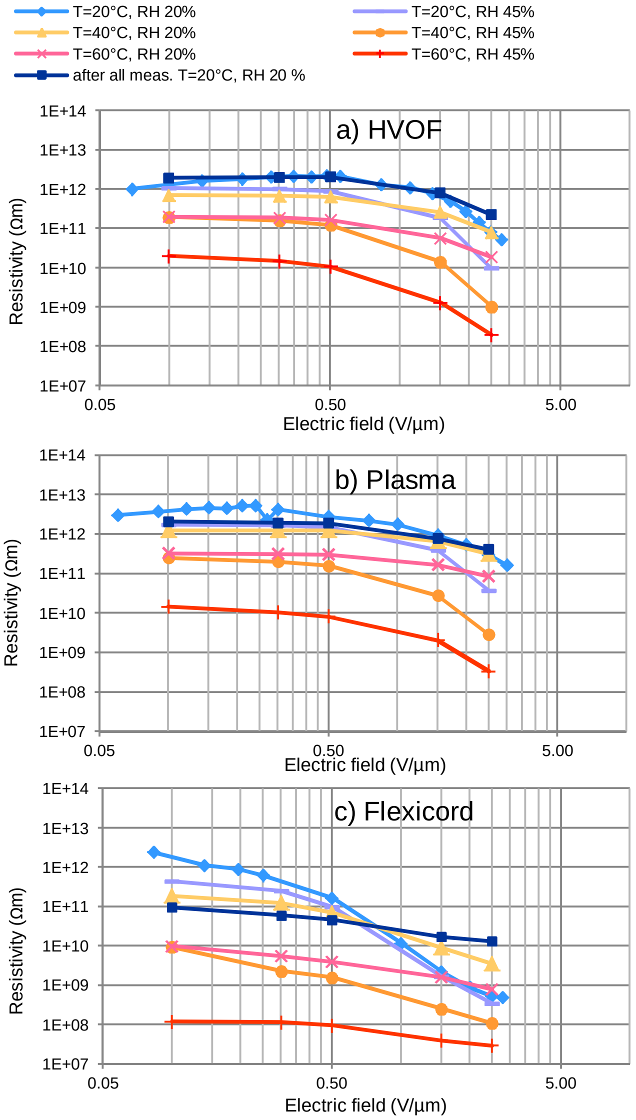

Fig. 1. DC resistivity of the studied coatings in all studied ambient conditions and after these measurements: a) HVOF sprayed, b) plasma sprayed and c) flame sprayed flexicord.

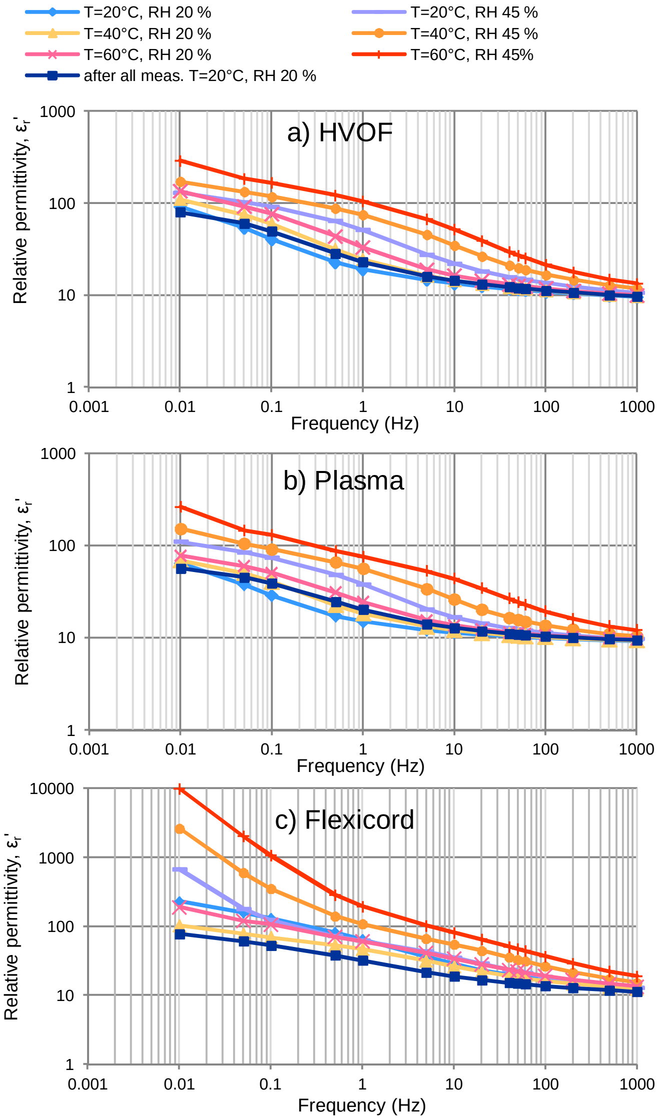

Fig. 2. Relative permittivity as a funtion a frequency for all studied coatings in all studied ambient conditions and after these measurements: a) HVOF sprayed, b) plasma sprayed and c) flame sprayed flexicord.

e.g. due to breakdowns in the interfaces inside the coating.

Loss index was also defined for all the materials. The behavior of the coatings was similar as the relative permittivity; the dielectric losses increased when the temperature increased and also the influence of relative humidity was similar. Flexicord had the highest dielectric losses whereas the HVOF had the lowest throughout the studied frequency range.

C. DC dielectric breakdown strength

Figure 3 presents the DC dielectric breakdown strength distribution of the studied spinel coatings along with the corresponding Weibull parameters. Typically, HVOF sprayed coatings have higher breakdown strength values than the coatings sprayed with other techniques due to the more dense structure of HVOF sprayed coatings. For this HVOF coating the mean was, anyhow, only 13.6 V/µm (SD=2.5 V/µm) while e.g. in [1] the mean dielectric strength of HVOF spinel coating was ~31 V/µm (thickness 200 µm). The reason of this is supposed to be the experimental powder used for HVOF coating.

In the case of the plasma and HVOF samples the similar Weibull β values indicate similar material homogeneities despite the differences in the raw materials and spraying techniques. However, the Flexicord sample shows even higher Weibull beta in comparison to the HVOF and plasma samples indicating even higher distribution homogeneity. If the weakest spot of Flexicord (8.4 V/µm) is excluded from the Weibull parameter calculation, the resulting α and β parameters are 18.5 V/µm and 15.9, respectively.

D. Discussion

DC resistivities of all the coatings are quite similar at low electric fields. Due to the special microstructure, hydrophilicity and slightly porous structure of thermally sprayed ceramic coatings, humidity can be absorbed in the coating. This can be seen in both the resistivity and dielectric spectroscopy results which show higher dependency on relative humidity than on temperature.

Like the humidity also the temperature has a clear influence on the dielectric properties, as increasing temperature decreases the DC resistivity and increases the relative permittivity and the dielectric losses. However, it is difficult to distinguish exactly the individual effects of temperature and humidity although quite good indications can be made based on the RH 20 % results. In any case it is obvious that the dielectric measurements of thermally sprayed ceramic coatings should be made at controlled conditions and good documentation of the measurements conditions is of significant importance.

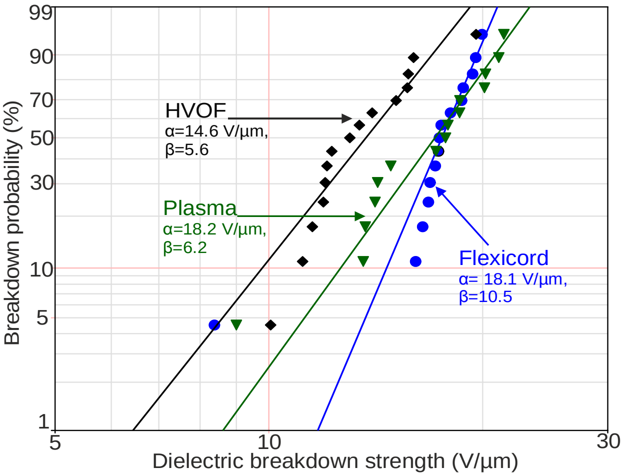

Fig. 3. The dielectric breakdown strength distribution of the studied coatings and the Weibull parameters α and β.

Flexicord had the highest porosity and dielectric strength but the lowest dc resistivity. HVOF and Plasma samples have lower porosities and breakdown strengths but higher dc resistivities in comparison to Flexicord. It may be speculated that the slightly higher conductance of Flexicord may form a more preferable charge distribution in the dielectric for DC strength and this way improve the fast rate-of-rise DC breakdown strength.

IV. CONCLUSIONS

In DC resistivity and dielectric spectroscopy measurements, the relative humidity has higher influence on the results than temperature. This can be linked to the coatings capability to absorb moisture. Thus, the dielectric measurements should be performed at carefully controlled conditions in order to be able to compare results to other studies. The highest DC breakdown strength was measured for flame sprayed Flexicord which had the lowest resistivity although more dense HVOF coatings typically has the highest dielectric strength. The main reason for this result is probably in the properties of the experimental powder used for HVOF coating.

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