Journal of the European Ceramic Society 21 (2001) 1685–1688
www.elsevier.com/locate/jeurceramsoc

Dielectric properties of plasma sprayed titanates

Pavel Ctibor [a,*], Josef Sedlacek [b]

[a] *Materials Engineering Department, Institute of Plasma Physics ASCR, 182 21 Prague 8, Czech Republic*
[b] *Department of Mechanics and Materials Science, Faculty of Electrical Engineering CTU, 166 27 Prague 6, Czech Republic*

Received 4 September 2000; received in revised form 23 October 2000; accepted 25 October 2000

Abstract

This paper presents the study of the dielectric properties of three plasma-deposited titanates. The deposits were prepared from powders with the same starting composition as industrially produced dielectric ceramics. Influence of plasma spraying itself and of the subsequent annealing of sprayed deposits on electric resistivity, permittivity and the loss factor is reported. Pure synthetic perovskite ($CaTiO_3$) and two perovskite-related ceramic materials ($MgTiO_3$–$CaTiO_3$ and $LaMg_{0.5}Ti_{0.5}O_3$–$CaTiO_3$) were plasma sprayed to form specimens enabling various electric measurements. $CaTiO_3$ and their solid solution with $LaMg_{0.5}Ti_{0.5}O_3$ have perovskite crystal structure and $MgTiO_3$ have the ilmenite structure. Water-stabilized plasma gun WSP® as well as commercial APS (gas stabilized system) were used to form ceramic layers on stainless steel substrates as well as self-supporting ceramic discs. Surface of specimens was ground after spraying. Thin layer of aluminum as the counter-electrode was sputtered in reduced pressure on the ground surface. Micrometric capacitor and ASTM-convenient resistivity adapter were used for voltage applying. Permittivity and volume resistivity were calculated from the measured capacity and resistance respectively. Self-supporting ceramic deposits were annealed at two different temperatures below and above the sintering temperature of the given material. Properties dependence on annealing temperature was obtained and discussed in relation to porosity. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Capacitors; Dielectric properties; Perovskites; Plasma spraying; Porosity

1. Introduction

In the last decades thermal spraying has become a well-accepted technology as a coating method for metallic and ceramic materials and has been used in a variety of fields. Plasma sprayed coatings are produced by the introduction of powder particles of a material into a plasma flame, which melts and propels them towards the substrate. The formation of a coating is the result of the interaction between a droplet and the substrate or the previously deposited layers. Among candidate materials for plasma spraying titanates $ATiO_3$, where A is an element from the alkaline earth group (II), were not systematically tested until the authors' recent work.[1,2] Titanates, in general, form a wide and important group of dielectric ceramics. Besides materials based on titanium oxide, studied materials represent the simplest linear dielectrics used for technical applications.

The synthetic form of $CaTiO_3$ produced by reactive sintering of CaO and TiO_2 was already reported in the 50-ties.[3,4] It is used for capacitors and other electric parts under various trade names, as Negatit 1500.[5] $CaTiO_3$ is characterized by the negative thermal polarization coefficient α_ε and it is often used in complex ceramic systems in which perovskite content changes temperature dependence of permittivity ε.

$MgTiO_3$ is one dielectric whose α_ϵ can be well controlled by the addition of $CaTiO_3$. Mixture of $MgTiO_3$ and $CaTiO_3$, with the ratio equal to 94:6 weight percent (in this paper the label MCT is used) has permittivity independent of temperature in a wide range of frequencies.[6] This material is used as a low-loss microwave dielectric in sintered state.

The next material from the family of microwave dielectrics is the solid solution of two titanates having perovskite crystal structure. One component is $CaTiO_3$ and the second component is $LaMg_{0,5}Ti_{0,5}O_3$. The

---

* Corresponding author. Tel.: +42-2-66-05-32-27; fax: +42-2-85-86-389.
E-mail address: ctibor@ipp.cas.cz (P. Ctibor).

PII: S0955-2219(01)00093-0

material is prepared from feedstock powder with 54 wt.% of $CaTiO_3$ and 46 wt.% of $LaMg_{0,5}Ti_{0,5}O_3$. Label LMT is used in this paper.

2. Experimental procedure

2.1. Sample manufacturing

Plasma spraying was performed by using a commercial gas-stabilized plasma (GSP) spray system P4-HB (Plasmatechnik, Switzerland) as well as by special high-throughput water-stabilized plasma (WSP®) system[7] patented by Institute of Plasma Physics ASCR. $CaTiO_3$ and MCT were processed by WSP® spraying, LMT by GSP spraying. Produced samples were in the form of ceramic layers on stainless steel substrates (GSP, WSP®) as well as self-supporting ceramic discs (WSP®).

Surface of specimens was ground after spraying to eliminate difference in surface roughness among both processes. A thin layer of aluminum as the counter-electrode was sputtered in reduced pressure on the ground surface.

Annealing of MCT self-supporting discs was done at 1250°C for 2 h, while temperature of bulk ceramics sintering from powder is approximately 1180°C. For comparison also annealing well bellow the sintering temperature was performed (680°C/0.5 h).

2.2. Electric measurements

Electric measurements were carried out 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).

Electric resistance was measured with a special adapter — model 6105 — to fulfill ASTM recommendations.[8] The electric field was applied by the regulated high-voltage supply and the values read by a multi-purpose electrometer (617C, Keithley Instruments, USA). Reference measurements were done by teraohmmeter operating in the range from 1MΩ up to 1TΩ (Tesla, Czech Rep.). Voltage was 100V DC in both cases. Volume resistivity was calculated from the measured resistance and specimen dimensions.[9]

Capacity was measured at frequency 1 kHz using a low-frequency LCR-meter (BM 595, Tesla, Czech Rep.) and at 1 MHz using programmable LCR-meter operating to 1 MHz (PM 6306, Fluke, Germany). Applied voltage was 1V AC, the stabilized electric source was equipped with a micrometric capacitor as recommended in the relevant standard.[10] 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 measured at the same frequencies as capacity.

3. Results and discussion

3.1. Permittivity

Permittivity results are shown in Table 1. Plasma deposits have much higher permittivity than sintered ceramics. These difference can be accounted for the water, absorbed within the voids.[11] But calculations show that the situation is more complicated. If we calculated the permittivity of a two-component system according to Lichtenecker laws or related formulas,[12,13] the presence of water in voids cannot explain the results. The two-component system (ceramics and water) must have the values of calculated permittivity between the values of its components. Relative permittivity 56 and 90 could be considered in the case of void-free LMT and H_2O respectively, but the measured value of the system is 173 at 1 kHz. The values for all studied materials are summarized in Table 1. All the measured values disagree with the above formulated necessary condition for the two-component system. The water adsorbed within the voids cannot be, therefore, responsible for pemittivity values of plasma deposited titanates.

For the calculation of the intrinsic permittivity of as-sprayed samples with zero porosity (i.e. void free) must be known. That is, of course, impossible because certain porosity is an inherent property of any plasma sprayed deposits. However, that value can be extrapolated from a dependence of calculated intrinsic permittivity on porosity [14] (see Fig. 1).

3.2. Loss factor

Measured values of the loss factor are summarized in Table 2. Losses in plasma-sprayed materials are much

Table 1
Relative permittivity of studied titanates

Material	Frequency (Hz)	Measured value — plasma-sprayed sample	Measured value — sintered sample	Porosity[a] (%)	Calculated value[b]
$CaTiO_3$	10^3	802	111	8.3	143
$CaTiO_3$	10^6	408	111	8.3	143
MCT	10^3	113	20	5.8	30
MCT	10^6	41	20	5.8	30
LMT	10^3	173	56	6.8	57.8
LMT	10^6	79	56	6.8	57.8

[a] Porosity of plasma-sprayed sample measured by image analysis.

[b] Calculated according to the Lichtenecker logarithmic formula.[12]

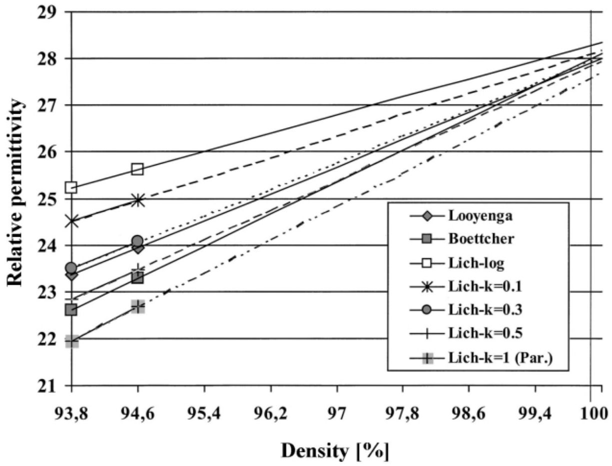

Fig. 1. Dependence of intrinsic permittivity on porosity at MCT plasma deposits.

Table 2
Loss factor of studied titanates (measured values are the averages from six samples)

Material	Frequency (Hz)	Plasma-sprayed (*P*)	Sintered (*S*)	Ratio *P*/*S*
$CaTiO_3$	10^3	0.23	0.0006	383.3
$CaTiO_3$	10^6	0.28	0.0006	466.6
MCT	10^3	0.32	0.0034	97.1
MCT	10^6	0.20	0.0014	142.9
LMT	10^3	0.042	0.0020	21.2
LMT	10^6	0.112	0.0005	224.6

Table 3
Volume resistivity (Ωm) (average values from min. six samples by plasma spraying and min. two samples by sintering); *Y*, literary value[15]

Material	Plasma-sprayed (*P*)	Sintered (*S*)	Ratio *P*/*S*
$CaTiO_3$	1.64×10^7	1.41×10^{12}	1.16×10^{-5}
MCT	1.17×10^7	7.54×10^{11}	1.55×10^{-5}
LMT	4.88×10^9	10^{12} Y	4.88×10^{-3}

higher than in sintered samples. Loss factor of plasma deposits (except of MCT) increases with increasing frequency, while an opposite tendency — small decrease of losses with increasing frequency — is typical for sintered ceramics [4,12] and was proved by sintered samples. The resistivity is not frequency-dependent but voltage-dependent. At room temperature only the electronic conduction mechanism could be expected in these materials.

3.3. Volume resistivity

The resistivity results are summarized in Table 3. Plasma deposits have approximately 10 000 times lower volume resistivity than sintered ceramics. This difference could be explained in similar way as permittivity.

Table 4
Annealed MCT plasma deposits

Parameter	680	1250	Sintered
Vol. res. (Ωm)	3.09×10^{11}	6.88×10^{12}	7.54×10^{11}
Permittivity at 10^3 Hz	21	22	20
Permittivity at 10^6 Hz	21	21	20
Loss factor at 10^3 Hz	0.079	0.005	0.0034
Loss factor at 10^6 Hz	0.019	0.003	0.0014

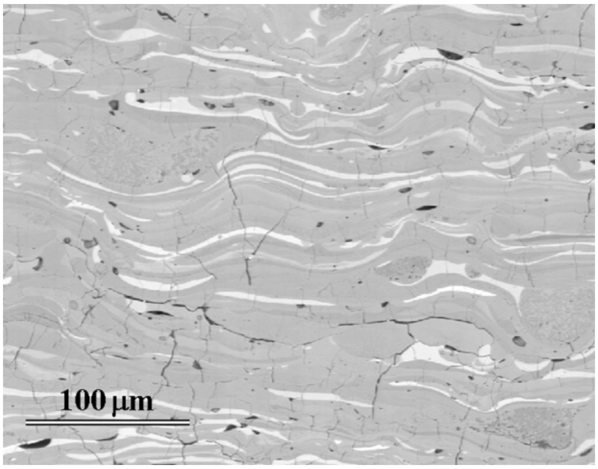

Fig. 2. Microstructure of as-sprayed MCT plasma deposit, SEM, BE, magnification 200×.

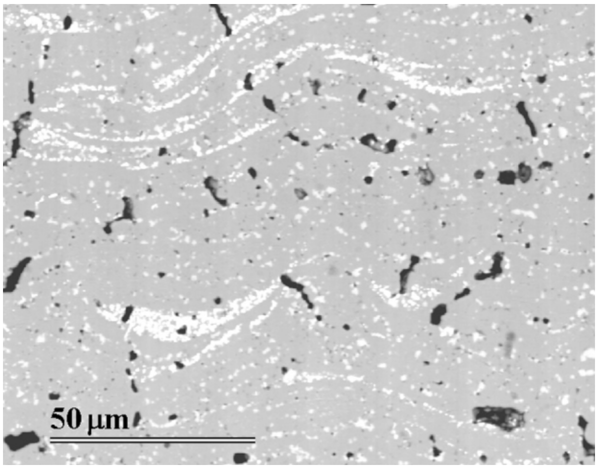

Fig. 3. Microstructure of MCT plasma deposit annealed at 1250°C/2 h, SEM, BE, magnification 500×.

3.4. Annealing and their influence on dielectric properties

Measured values are summarized in Table 4. It can be seen, that annealing of MCT at 680°C leads to balancing of permittivity value to the sintered ceramics. Resistivity remains relatively low but it has definitely increased in comparison with the as-sprayed deposits (see the structure — Fig. 2). Therefore the loss factor is relatively high after annealing at 680°C, but lower than at as-sprayed deposit. Annealing above the sintering temperature (i.e. at 1250°C, see the structure — Fig. 3). gives all three parameters at the same level as for sintered ceramics, while resistivity overgrows the value of sintered MCT.

4. Conclusions

Basic dielectric properties of three plasma-sprayed titanates were studied. Results were compared with values measured by the same instrumental set-ups on specimens produced by conventional sintering technology and literary values were also used for comparison.

It was found that as-sprayed plasma-deposits exhibit extraordinary differences from sintered ceramics in all studied parameters. These differences could be a consequence of the unique microstructure of plasma deposits.[16] It is shown that water adsorbed in pores cannot account for the differences in the as-sprayed and sintered samples, as suggested in the literature.[11] This conclusion is based on calculations performed according to formulas describing dielectric material as a mixture of ceramics and a medium filling the voids. Moreover, this conclusion is supported by results on annealed plasma deposits. Porosity did not change significantly after annealing, but dielectric behavior does. Plasma deposits annealed above the sintering temperature of the given material were found as dielectrics fully comparable with sintered ceramics and therefore useful in industrial application. A patent application is pending.

Physical nature of observed behavior of plasma deposits is a challenge for future research. Measurements at elevated temperatures as well as construction of relaxing curves and looking for resonance frequencies are in progress. Measurement of the dielectric strength of plasma-sprayed titanates is also desirable.

Acknowledgements

This work was supported by the Academy of Sciences of the Czech Republic project No. AV K 1010601/97. The authors thank K. Neufuss and J. Kubicek for plasma spraying, to J. Fiedlerova and V. Kotek for sintering, and J. Machut for providing some measurement facility.

References

1. Ctibor, P. et al., Plasma spraying of titanates — I. In *Proceedings of the 1st International Thermal Spay Conference*, ed. C. Berndt. ASM International, Materials Park, OH, USA, 2000, pp. 945–950.
2. Ctibor, P. et al., Plasma spraying as a technique for dielectric ceramics preparation. In *Proceedings of the 9th International Conference 'METAL 2000'*, Tanger s.r.o., 2000, Abstract at p. 75, Fulltext on the CD-ROM under No. 514.
3. Bohrer, R., *Gmelin Handbook of Inorganic Chemistry*, Vols. 41–42, Leipzig, 1951 (in German).
4. Landolt, H. and Boernstein, R., *Values and Functions in Physics, Chemistry, Astronomy, Geophysics and Technology*, Vol. IV, Part 3. Springer Verlag, Berlin, 1957 (in German).
5. Supplement of the Czech standard CSN 72 5835, Ceramic materials 835. Czech Institute for standardization, Praha, 1964 (in Czech).
6. Bauer, A., Technology and Application of Ferroelectrics, Leipzig, 1976 (in German).
7. Chraska, P. and Hrabovsky, M., An overview of water stabilized plasma guns and their applications. In *Proceedings of the International Thermal Spray Conference*, ed. C. Berndt. Orlando, FL, 1992, pp. 81–85.
8. US standard ASTM D 257-66.
9. Cibor, P. and Sedlacek, J., Electric resistivity of ceramic plasma deposits. In *Proceedings of Workshop 2000-CTU Reports*, Part A. CTU in Prague, Praha, 2000, p. 242.
10. Czech standard CSN IEC 250. Czech Institute for standardization, Praha, 1997 (in Czech).
11. Pawlowski, L., The relationship between structure and dielectric properties in plasma-sprayed alumina coatings. *Surface and Coating Technology*, 1988, **35**, 285–298.
12. Koller, A., *Structure and Properties of Ceramics*. Elsevier, London, 1994.
13. Lichtenecker, K., The electric resistance of synthetic and natural multi-component systems. *Physikalische Zeitschrift*, 1924, **25**(8), pp. 169–233 (in German).
14. Koblizek, V., Contribution to the analytic expression of permittivity of elastomer foams. *Acta Polytechnica-Works of CTU in Prague*, 1980, **13**(3), pp. 49–59 (in Czech).
15. Schwarzbach, J., Ceramic low-loss dielectric with certain temperature coefficient of capacity, Patent No.149524, 1973 (in Czech).
16. Ilavský, J. et al., Use of small-angle neutron scattering for the characterization of anisotropic structures produced by thermal spraying. *Ceramics — Silikaty*, 1998, **42**(3), 81–89.