České vysoké učení technické v Praze
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Plazmové nástřiky titaninIčitanů a testování jejich využitelnosti v elektrotechnice

Plasma sprayed titanates and testing of their applicability for electrical engineering

Summary

The lecture is focused on plasma sprayed ceramic materials that are in sintered form used in electrical engineering. Processing of these materials by plasma spray technique is a challenge for understanding the phenomena involved in modifications of microstructure, crystallographic structure and electronic states inherently connected with this technology. The addressed materials are titanates, namely $CaTiO_3$, its mixture with $MgTiO_3$, pure $BaTiO_3$ and finally the chemically (apparently) simplest material, titanium dioxide TiO_2. The run of two- step process consisting of plasma spraying and subsequent annealing (thermal post-treatment) for preparation of ceramic layers having electrical characteristic comparable with sintered ceramics is discussed. The plasma spraying is able to cover large and variously shaped substrates and by this way it broadens the possibilities of performing ceramic components for electrical engineering.

Souhrn

Přednáška je zaměřena na plazmově stříkané keramické materiály, které jsou ve slinuté podobě využívány v elektrotechnice. Zpracování těchto materiálů pomocí plazmového nanášení je výzvou pro porozumění jevům souvisejícím se změnami mikrostruktury, krystalografické struktury a stavů elektronů, které jsou nedílně svázány s použitou technologií. Zkoumanými materiály jsou titaničitany, zejména $CaTiO_3$, jeho směs s $MgTiO_3$, dále čistý $BaTiO_3$ a na závěr materiál (zdánlivě) chemicky nejjednodušší, TiO_2. Je diskutován průběh dvou-krokového výrobního procesu, skládajícího se z nástřiku a následného tepelného zpracování, pro přípravu keramických vrstev majících elektrické vlastnosti srovnatelné se slinutou keramikou. Plazmovým nástřikem lze pokrýt rozměrné a nejrůzněji tvarované povrchy rozličných materiálů a díky tomu tato technologie rozšiřuje možnosti výroby keramických součástek pro elektrotechniku.

Keywords

Plasma spraying; annealing; titanates; dielectrics

Klíčová slova

Plazmové stříkání; žíhání; titaničitany; dielektrika

Obsah / Content

Chapter 1

Introduction

Plasma spraying is a thick-coating production technique where a coating builds not atom-after-atom or molecule-after-molecule like thin films, but pieces of a powder with size typically tens of micrometers are the coating building units. These are molten by plasma jet and propelled towards the substrate. The powder melting is often accompanied by certain degree of unwanted evaporation and the melting/cooling cycle is extremely rapid. Some compounds with a complicated chemical composition tend to decomposition and preferable evaporation of only certain constituents. For this reason, chemical engineering of materials is possible in limited extent and the spray technique needs working with materials having relatively simple composition, i.e. instead of $Ba[Ti_{1-x}(Ni_{1/2}W_{1/2})_x]O_3$ [1] it should be simple $BaTiO_3$. In another case the chemical composition of the final product could be dramatically changed. Example of such a material – very hardly processable with thermal spray – is lead zirconate titanate, labeled PZT, c.f. Chapter 2.

Plasma spray process provides parameters by which the structure and properties of the coating could be tailored – electrical power, stand-off distance of the substrate, feeding distance of the powder, preheating / cooling of the substrate, shrouding (i.e. protection to ambient air) and powde size distribution. By testing the coating we gain knowledge useful for process parameters modification to improve the coating quality. The homogeneity, porosity etc. of plasma spray coatings are typically worse than in bulk sintered ceramics but the lamellar structure of coating offers interesting characteristics (like e.g. low thermal conductivity).

There was observed that plasma-sprayed titanates exhibit a strong relaxation of dielectric relative permittivity when they are measured in the as-sprayed state. The loss factor of as-sprayed deposits has exactly the same character of frequency dependence as the relative permittivity, i.e. strong decrease with increasing frequency. This character of losses corresponds with general trends, but the absolute values are much higher in the studied case of plasma deposits. The frequency-dependence of those properties is preserved in $CaTiO_3$ as well as in $MgTiO_3$-$CaTiO_3$ plasma deposits. The volume electrical resistivity of the samples in a plasma sprayed state is significantly lower than in a sintered state. To anneal the sprayed deposits, annealing temperature about 0.6 T_s, where T_s is sintering temperature (considered to be 0.7 of the melting point), was proven as efficient enough. The annealing of plasma deposits at temperatures slightly below the sintering temperature is a promising way to prepare ceramics whose dielectric characteristics are more or less the same as for the sintered bulk form of the same material. The plasma spraying broadens technological variability in the field of dielectric ceramics.

Chapter 2

$CaTiO_3$ and MCT

Calcium titanate ($CaTiO_3$) is one of the alkaline earth titanates like barium titanate ($BaTiO_3$), magnesium titanate ($MgTiO_3$) and strontium titanate ($SrTiO_3$). These titanates have recently attracted attention because they are used as i.e. ferroelectric, semi-conductive, photorefractive materials and catalysts [**1**]. Dielectrics based on calcium titanate are widely used in different fields of electronics applications [**2–4**]. For its high relative permittivity and low dielectric losses $CaTiO_3$ is recommended also for microwave applications [**5,8**]. Sintered dielectric ceramics are used for production of a variety of components such as oscillators, filters and resonators for microwave systems.

In the plasma sprayed $CaTiO_3$ an amorphous fraction was observed. In our older paper [**6**] no amorphous fraction was detected because of use of the Siemens D 500 XRD instrument and old evaluation software. Using the new XRD equipment Bruker D8 Discover an amorphous fraction was monitored. The starting powder was fully crystalline orthorhombic $CaTiO_3$ (Powder Diffraction File card 22-153), the coating contained some amorphous proportion whereas majority of the material was again orthorhombic $CaTiO_3$, and finally annealed coatings were all composed from fully crystalline orthorhombic $CaTiO_3$. For the difference between dielectric behavior of coatings annealed to various temperatures the different degree of healing of the microstructural defects (i.e. closing of thin cracks and finest pores) was responsible. Example of such structural changes is provided in Fig. 8 in our recent paper on this topic [**7**].

Annealing temperature 1010°C, equal to 0.7 of the sintering temperature, was proven to be high enough to turn the dielectric properties to values (relative permittivity 135, loss factor 0.005, volume resistivity $5x10^{10}$ to $6x10^{10}$ Ωm) typical for well sintered $CaTiO_3$ ceramics. At the HT-XRD, above the temperature of 1010°C the structural model of orthorhombic $CaTiO_3$ (*Pbnm* space group) was not valid, and tetragonal $CaTiO_3$ (I4/mcm space group) was more suitable. Amorphous component, which was observed in the as-sprayed state, affects the mobility of ions in the structure. At very low frequencies this plays an important role and causes the high permittivity at simultaneously high loss factor and low resistivity. – The results concerning $CaTiO_3$ are relevant for plasma spray techniques WSP and GSP [**6,7**].

Magnesium titanate ($MgTiO_3$) is one dielectric whose temperature coefficient of permittivity (expressed in ppm/°C) 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 (the label MCT is used) has permittivity independent of temperature in a wide range of frequencies. This material is often used as a low-loss microwave dielectric in the sintered state.

Annealing temperature 750°C, equal to 0.6 of the sintering temperature [**6,8**], was proven to be high enough to turn the dielectric properties to values (rel. perm. 22, loss factor 0.005, vol. resist. 7×10^{12} Ωm [**9**]) typical for well sintered MCT ceramics. Healing of the microstructural defects (i.e. closing of thin cracks and finest pores) was mentioned as the main factor responsible for the turn of the dielectric properties to the sintered-like values. Besides MCT, also other phases were detected in the annealed coatings (as Mg_2TiO_4 and $MgTi_2O_5$), so their effect on dielectric properties is difficult to be separated from the effect of microstructure healing and other possible effects (c.f. the chapter dealing with $BaTiO_3$). – The results concerning MCT are relevant for plasma spray technique WSP [**6,9**].

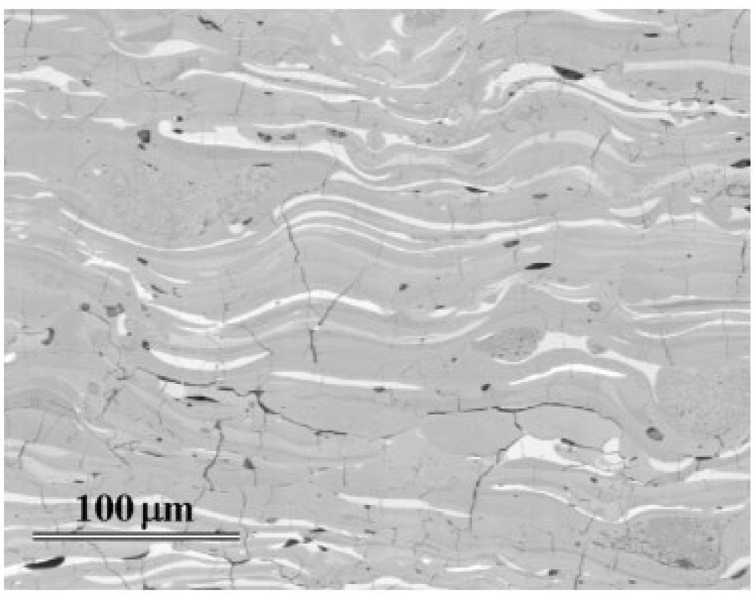


Fig. 1: Microstructure of as-sprayed MCT plasma deposit, SEM-BE.

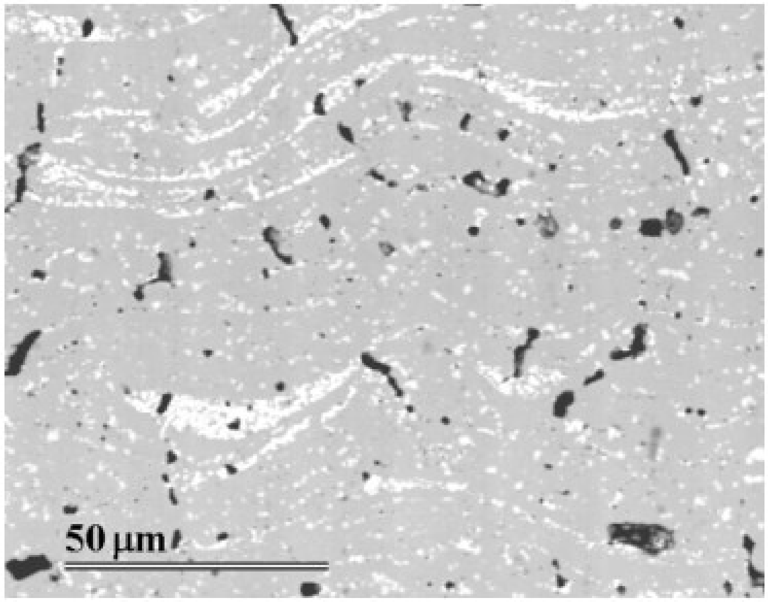


Fig. 2: Microstructure of MCT plasma deposit annealed at 1250°C/2h, SEM-BE.

Chapter 3

$BaTiO_3$

In recent years, the development of lead-free piezoelectric ceramics has been extensively investigated in order to find an alternative for toxic lead zirconate titanate (PZT). Among the candidates, barium titanate ($BaTiO_3$), which is a dielectric material for capacitor application nowadays (most typically as one constituent of a system with other oxides), has an important role. $BaTiO_3$ is a multifunctional oxide that exhibits complex phase appearance. Between 120 °C (393 K) and 1457 °C (1730 K) $BaTiO_3$ has a cubic perovskite structure that consists of corner linked oxygen octahedra containing Ti^{4+}, with Ba^{2+} ions. Cooling below 120 °C results in small displacements in the positions of the cations in the unit cell, resulting in polar ferroelectric phase (crystallografically considered as tetragonal), existing in the temperature interval between 5 °C (278 K) and 120 °C [**10**].

Dielectric properties of plasma sprayed $BaTiO_3$ at room temperature (rel. perm. 400, loss factor 0.3, vol. resist. 7.5×10^4 Ωm [**11**]) indicated rather conductor-like behavior. Until 200 °C, which was our maximum available measurement temperature, no change in order of magnitude was observed versus the R.T. values. Therefore the conclusion was drawn that plasma sprayed $BaTiO_3$ does not exhibit the tetragonal-to-cubic (t–c) phase transformation. This result was confirmed by three other techniques, RUS, DSC and HT-XRD [**11**].

Annealing temperature 750°C, equal to 0.65 of the sintering temperature [**12**], was proven to be high enough to turn the dielectric properties to values (rel. perm. 180, loss factor 0.05, vol. resist. $3x10^{11}$ Ωm [**12**]) that are typical for a general group of sintered dielectrics. Well sintered $BaTiO_3$ however exhibit a broad range of the listed properties, sensitively dependent on grain size and grain boundary tailoring – so a direct comparison is not provided. Healing of the microstructural defects was mentioned as the main factor responsible for the turn of the dielectric properties to the sintered-like values. Besides crystalline $BaTiO_3$, also an amorphous phase, quantified by XRD to be about 5 %, was present in the annealed samples. Its effect on dielectric properties is difficult to be separated from the effect of microstructure healing.

As another possible effect was identified the presence of oxygen vacancies in the coatings, present in the as-sprayed state and remaining partly even after annealing, as the color of the samples and band gap, calculated from a diffuse reflectance, indicated. Recently, by means of positron annihilation spectroscopy (PAS) was verified a difference in vacancies concentration between as-sprayed and annealed $BaTiO_3$ coatings [unpublished research]. – The results concerning $BaTiO_3$ are relevant for plasma spray technique GSP [**11,12**].

Recently sprayed $BaTiO_3$ by a novel WSP-H technique [**13**], however, exhibited already in the as-sprayed state very interesting dielectric properties (rel. perm. 300, loss factor 0.015, vol. resist. $6x10^{11}$ Ωm [unpublished research]). The difference of WSP-H versus GSP is due to higher velocity and temperature of the particles in flight (i.e. inside the plasma jet) [unpublished research].

The low annealing temperature, always proven (for $CaTiO_3$, MCT and $BaTiO_3$) to be high enough to turn the dielectric properties to values typical for sintered dielectrics, is due to “stored” energy in the material. This is represented with nanometric crystallites (e.g. 65 nm to 140 nm for as-sprayed and variously annealed $BaTiO_3$ [unpublished research]). The nanometric crystallites present enhanced sinterability and tendency to rearrange itself, but not to overgrow, and by this way they heal the microstructure defects at lower temperature then the conventional sintering powders.

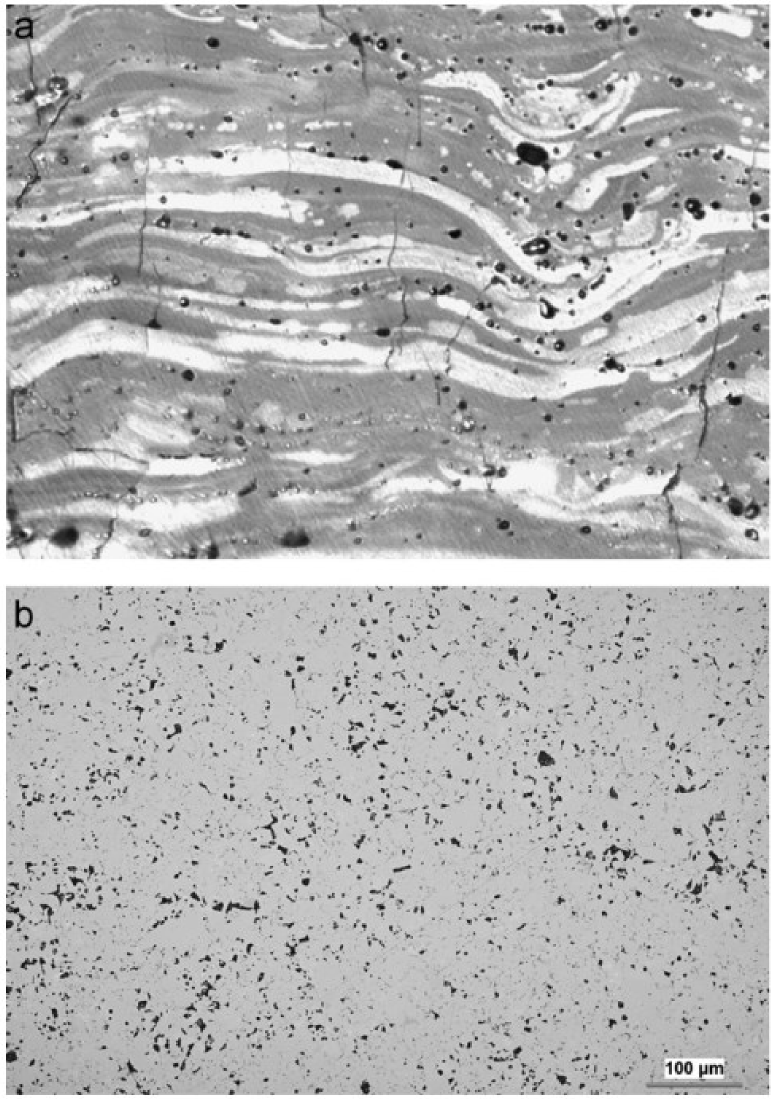


Fig. 3: Microstructure of $BaTiO_3$ plasma deposit (a) and bulk ceramics (b), light microscopy (both in the same magnification).

Chapter 4

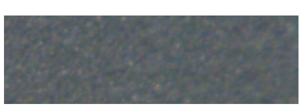
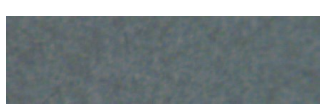
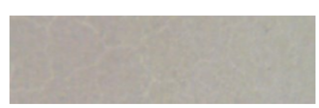
TiO_2

Titanium dioxide (TiO_2) has many applications, namely in photo-catalytic, dielectric and optical-coating components. Titanium dioxide is one of the most important photocatalysts used for such applications. From this viewpoint it was also in focus of our research. Electrical aspects of its behavior were studied with slightly lesser effort, but they gave us also important information.

TiO_2 begins to lose oxygen at a temperature above 1600 °C in reductive as well as neutral atmospheres. The partial pressure of oxygen required to reduce TiO_2 to Ti_2O_3, Ti_3O_5 or Ti_4O_7 is of the order of 10^{-5} Pa at around 2000 °C. Oxygen-deficient phases of TiO_2 (especially Ti_3O_5, Ti_6O_{11}) are sometimes observed in the coatings by XRD, especially when the feedstock is an agglomerated titania nanometric powder [**14**], as is it also in majority of our experiments. In thermally sprayed TiO_2 the result of interaction of the initial (stoichiometric) TiO_2 powder with plasma is formation of reduced TiO_x (where X<2). These oxygen-depleted coatings are conductive with volume resistivity only up to 1500 Ωm [**15-17**]. Oxygen vacancies introduced changes in band gap when Ti^{4+} and Ti^{3+} ions interact and free movement of electrons is allowed.

Annealing temperature 760 °C equal to 0.6 of the sintering temperature [**16**] was proven to be high enough to turn the dielectric properties to values (rel. perm. 100, loss factor 0.05, vol. resist. 1.3×10^9 Ωm) typical for sintered TiO_2 ceramics. XRD analysis verified the presence of single rutile phase TiO_2 in the starting powder, coatings and annealed coatings as well. Healing of the microstructural defects was one of the factors responsible for the turn of the dielectric properties to the sintered-like values.

Table 1: Volume resistivity and surface color of the TiO_2 coatings [**16**]

Coating	**As-sprayed**	**Annealed 500°C**	**Annealed 760°C**
Volume resisti-vity [Ωm]	1040	3.19	1.3×10^9
Surface color			

Similar dielectric properties (rel. perm. 100 to 180, loss factor 0.05, vol. resist. 4.3×10^9 Ωm [**17**]) were recently found also for extremely thick (15 mm) plasma spray deposit annealed at much higher temperature, 1100 °C. Here XRD pattern of the feedstock powder corresponded to rutile TiO_2 with traces of Ti_3O_5 and quartz SiO_2. Pseudo-brookite phase of TiO_2 was detected by XRD in the deposit (4.7 %) and also after annealing (2.0 %), the rest being rutile.

However, in all the studied cases of TiO_2, the main factor responsible for the turn of the dielectric properties to the sintered-like values is the restoration of the depleted stoichiometry thanks to air atmosphere during annealing.

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Reviewing He performed many tens of reviews of papers for journals like Journal of the European Ceramics Society, Surface & Coatings Technology, Surface Engineering, Materials Science and Engineering B, Thin Solid Films, Journal of Electroceramics, Ceramics International and other.

Teaching He participates on Materials for Power Electrical Engineering (AE1B13MVE), Materiály pro výkonovou elektrotechniku (A1B13MVE), Nanotechnology (A0B13NNT) and other subjects.

Leader of projects

2000-2003 - Kontinuální plazmochemická syntéza karbidu boru, 104/01/0149, GAČR

2005-2008 - Progresivní žárové nástřiky odolné proti otěru, CV1QS200430560, GA AVČR

2008-2010 - Studium vlivu dopantů na fotokatalytickou aktivitu plazmově nanesených vrstev oxidů titanu, IAAX00430803, GA AVČR

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