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Electrophoretic deposition and sintering of zirconia layers on microstructured steel substrates

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Abstract

A method is developed to electrophoretically deposit homogeneous zirconia layers with a thickness of about 5 μm on microstructured steel substrates. To realize layers in this range of thickness, the use of fine to submicron zirconia powder is necessary. To determine the electrokinetic behavior of the powder particles during electrophoresis, their electrophoretic mobility (EM) is measured. Special attention is drawn to the dependence of the mobility on particle size, where Henry theory can be applied. After depositing the layer on the substrate, it is sintered at 1000 °C and investigated by optical microscopy and SEM.

Keywords: Electrophoresis; ZrO_2; Functional applications; Substrates; Steel; Coatings

1. Introduction

Thin ceramic layers can be useful in various applications like piezoceramic layers on silicon substrates for sensors or porous catalytic layers for micro reaction applications. In addition, in the field of micro process engineering thin protective layers of ceramics are appreciated to avoid corrosion of the metallic substrates.

Amongst other processes to deposit thin layers like PVD or CVD, or sol–gel processes, the electrophoretic deposition (EPD) is an appropriate method, because of the cost-effective and easy production of ceramic layers on electrically conducting substrates. Another advantage is, that even with suspensions of nanoscaled powders with low solids content (e.g. a few volume percent) deposits with satisfactory high green density are achievable.

The work at hand is aimed at electrophoretically depositing thin ceramic layers as corrosion protection on microstructured metallic substrates that are used as heat exchangers in micro process engineering. To deposit thin layers with a thickness of a few microns it is inevitable to use accordingly small particles in the nanometer range. Because of its chemical inertness and availability of submicron powders, zirconia is chosen as material for deposition. Furthermore, the use of nanoscaled particles has the advantage of lower sintering temperatures (as low as 1000 °C), which is important to avoid any thermally activated processes like annealing or recrystallization in the steel substrate. The idea of electrophoretically depositing a layer with subsequent sintering on a metal substrate is not new,[1] but still desirable to be implemented on microstructured substrates. The conflict between a high temperature needed for sintering and a low temperature needed to avoid any thermally effect on the substrate can also be overcome by laser processing after sintering.[2]

Electrophoresis is realized by applying an electrical field across the suspension, whereby electrically charged particles move to one electrode (the microstructured substrate) and are deposited there. As electrophoretic deposition requires stable ceramic suspensions, electrostatically stabilized aqueous suspensions are characterized regarding pH-value, electrical suspension conductivity, particle size distribution and electrophoretic mobility (EM). Furthermore, attention is drawn

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to the dependence of particle size on EM. Different particle size fractions, which can be produced by sedimentation, are analyzed regarding their EM.

2. Theory

The stabilization of ceramic suspensions can be achieved by methods of electrostatic or steric stabilization, or by a combination of both methods.[3–6] Electrostatic stabilization, which has been used for this work, occurs when the surface charge of the particles is influenced in a way that all particles have identical positive or negative charge high enough to repel each other. In aqueous suspensions this can easily be achieved by adjusting the pH-value of the suspension.

The surface charge results in a zeta-potential. There are several theoretical approaches to calculate the zeta-potential. The most general description is the Henry equation[4]:

$$\zeta = \mu \frac{\eta}{\varepsilon_0 \varepsilon_r} f_{\kappa r} \tag{1}$$

where ζ is the zeta-potential, μ the electrophoretic mobility, η the viscosity of the suspension, ε_0 the dielectric constant, ε_r the dielectric number and $f_{\kappa r}$ the Henry correction function. The mobility μ can be described by:

$$\mu = \frac{v}{E} \tag{2}$$

The velocity v of the particles after applying an electric field across a capillary cell containing suspended particles can be measured by laser Doppler anemometry.[7]

The Henry correction term is a function of κr, where r is the particle radius and κ the Debye–Hückel parameter and is dependent on the ionic strength of the suspension. This parameter is the inverse thickness of the particle's electrical double layer. The more ions are in vicinity of the particle, the thinner is the double layer. Derived from the Henry equation, in the assumption of Helmholtz and Smoluchowski[4,5] relatively large particles are considered in a merely ionic medium (values of $\kappa r > 100$). This leads to the Helmholtz–Smoluchowski (HS) equation, where the Henry term $f_{\kappa r}$ equals one. For very low values of $\kappa r < 0.1$, the Debye–Hückel (DH) equation can be applied, where $f_{\kappa r}$ becomes 1.5. The values between these boundaries can be calculated.[8]

The effects that dominate the characteristics of the Henry correction term in the regime between HS and DH are the electrophoretic retardation and the relaxation effect.[3,4] While moving, the particle strips off a part of its double layer that is retarded in the suspension. Small particles with large double layers show this effect (in the regime of DH-theory). The relaxation effect also decelerates the particle. Due to movement of the particle and retardation of the double layer, the center of charge of the particle is ahead of the center of charge of the double layer. This charge asymmetry can slow down the particle drastically, especially for high zeta-potentials. Therefore, it is obvious that the mobility of the particles depends on their size.

3. Experimental procedure

To produce a suspension, ceramic powder is weighed into a beaker together with de-ionized water as dispersion medium. The material used is zirconia powder, stabilized with 5 mol% yttria (Unitec PYT05.0-001H, UCM Group PLC, Stafford, Great Britain, named UNI1). For analysis of electrophoretic mobility, suspensions with a coarser powder (Unitec PYT05.005H, named UNI5) are prepared. The theoretical densities of the powders are 6.05 g/cm^3, the refractive index, important for particle size analysis, is 2.2 real and 0.01 imaginary index. The specific surface is 12.61 m^2/g for UNI1 and 4.56 m^2/g for UNI5.

After dispersing the powder in water, 0.1 M hydrochloric acid (HCl) is added to adjust the pH-value in the range between ca. 3 and 7 to analyze its effects on deposition. Influences of solids content, varied between 1 and 8 vol%, are also analyzed.

The dispersion of the suspension is carried out by ultrasonic treatment (Branson Sonifier W 450) with 60% ultrasonic amplitude and total duration of 5–20 min (50% duty cycle). The pH-value and electrical suspension conductivity are measured afterwards (pH-value measured with inoLab pH Level 2 gauging station and SenTix HW pH-probe, WTW, Weilheim, Germany, conductivity measured with conducting meter 703, Knick, Berlin, Germany).

The particle size distribution is analyzed by laser light scattering and polarization intensity differential scattering (PIDS) with LS230 (Beckmann Coulter, Krefeld, Germany). Density and refractive index are set for measurement of zirconia in water. For particle size distribution measurements, the suspension has to be diluted to an appropriate value.

Electrophoretic mobility is measured with the ZetaSizer 3000 HSa (Malvern Instruments, Herrenberg, Germany). For measurement it is necessary to dilute the suspension to a solids content of about 10^{-5} volume fraction. To analyze different particle size fractions from the same powder, the suspension is exposed to a sedimentation procedure in the Varifuge 3.0 RS (Heraeus Instruments, Hanau, Germany). Time and revolution of centrifugation are varied to get different particle size fractions from the coarse zirconia powder UNI5.

The electrophoretic deposition is carried out with a three electrode system with a Jaissle Potentiostat/Galvanostat 1002 PC.T (Waiblingen, Germany). The reference electrode (RE) is placed aside of both counter and working electrode (CE and WE), which are opposite to each other in a distance of 15 mm. The size of counter and working electrodes is 14 mm × 14 mm, but only the lower halves of both electrodes are immersed in the suspension. The counter electrode is a steel plate, the working electrode is the microstructured steel substrate, on which the layer is being deposited. The

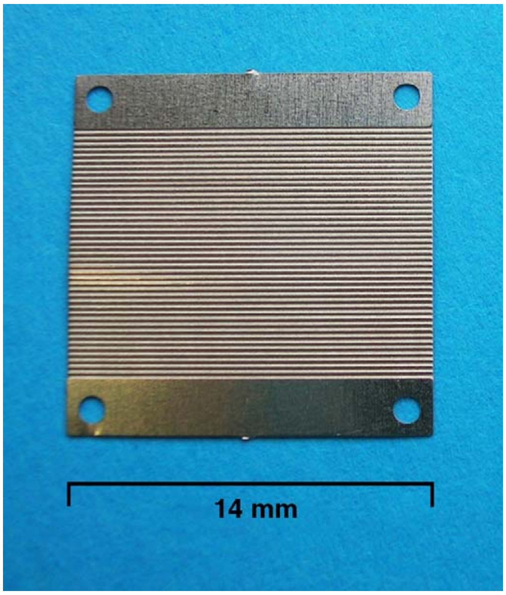

Fig. 1. Microstructured steel substrate.

structure of the substrate (Figs. 1 and 2) consists of rounded microtrenches with 160 μm width, 65 μm base width and 40 μm depth. The applied potential of the working electrode with respect to the suspension potential and the duration of EPD are varied. Due to positive particle charge, the applied potential is negative. The absolute potential is kept well below 1.5 V to prevent electrolysis of water. For the duration of EPD, deposition times in the range of a few seconds to several minutes are used.

After EPD, the substrate is taken out of the suspension and dried in horizontal position in a vacuum chamber. Sintering is performed in a sintering furnace CWF 1300 (Carbolite, Ubstadt-Weier, Germany). Sintering time and temperature are varied between 15 and 60 min at 900–1100 °C to receive optimum results.

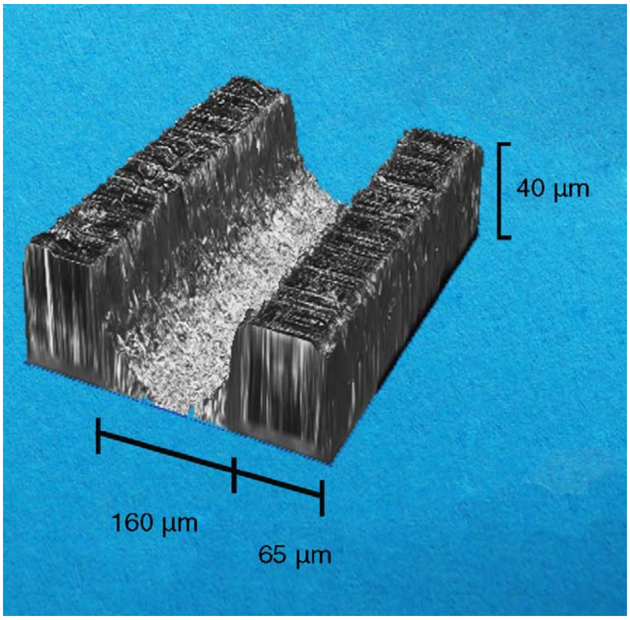

Fig. 2. Dimensions of structure trench.

The coated substrates and cross-sections are characterized using reflected light optical microscopy (RLOM) and scanning electron microscopy (SEM).

4. Results and discussion

A UNI1 suspension is prepared at pH-value ∼6 for particle size distribution measurement. Time of ultrasonic treatment is successively increased. Results are shown in Fig. 3. It can be seen that after 20 min there is still a 10 volume percent remnant of particle aggregates larger than 1 μm. However, the dominating fraction with 70 volume percent has a diameter smaller than 80 nm. The particle size distribution of UNI5 after ultrasonic treatment (5 min at 60% amplitude) is shown in Fig. 4. The distribution after centrifugation (20 min at 1000 rpm) is also illustrated.

The electrophoretic mobilities (EM) and thus resulting zeta-potentials calculated by Helmholtz–Smoluchowski and Debye–Hückel theory for UNI1 and two UNI5 fractions are shown in Fig. 5. The values for the zeta-potentials are

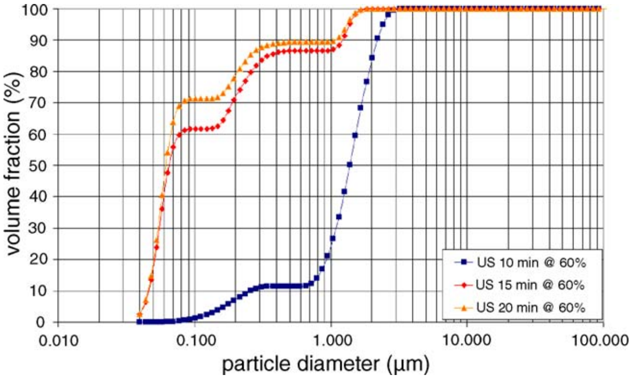

Fig. 3. Particle size distribution of UNI1 after ultrasonic treatment.

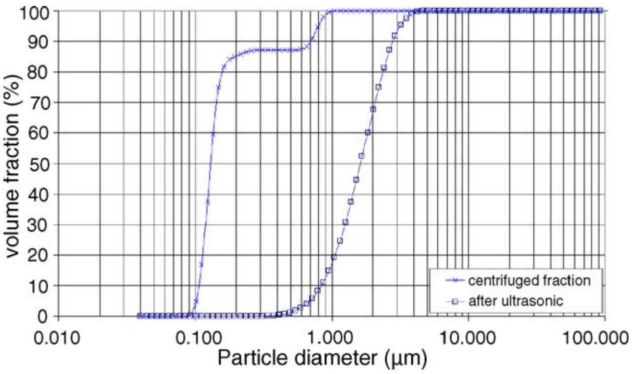

Fig. 4. Particle size distribution of UNI5 before and after centrifugation.

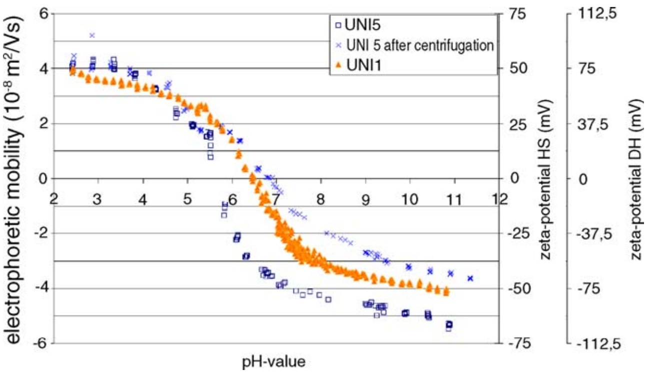

Fig. 5. Electrophoretic mobilities and zeta-potentials of UNI1 and UNI5 fractions.

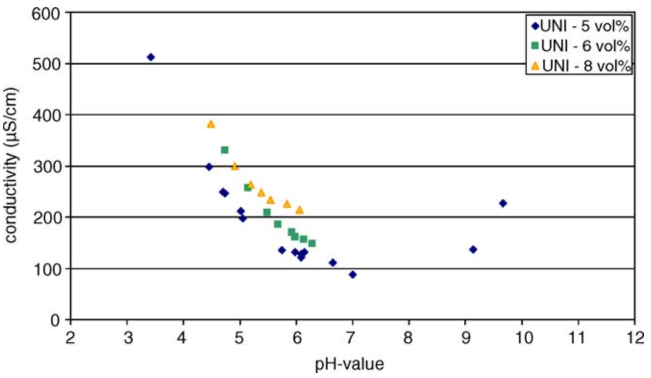

Fig. 6. Dependence of conductivity on pH-value for UNI1 suspensions with different solids content.

plotted just for orientation, actually measured is only the EM.

Especially in alkaline media it can be seen that the three fractions show different values of EM. At pH-values 9–11 the EM of the coarse UNI5 fraction (ca. -4.5 to -5.5×10^{-8} m^2/V s) is about 1.5 times the EM of the fine fraction after centrifugation (ca. -3 to -3.5×10^{-8} m^2/V s). If assumed that the values for κr are near the transition from HS to DH theory for the coarse and fine particles, respectively, this discrepancy between the values can be explained. In this case, no difference in zeta-potential would occur. The trend of UNI1 can be explained the same way, when – regarding to the measurement – the aggregates of the suspension dominate the fine particles (see Fig. 3). Unfortunately, until now these particle size dependant effects could not be exploited in the present application.

Suspensions for EPD are stabilized in acidic media. Considering only stabilization criteria, a pH-value of about four or less would be optimal (see Fig. 5). But for EPD, another effect has to be taken into account: The electrical conductivity of the suspension.[9–11] If a certain amount of electrical suspension conductivity is reached, the current is rather transported through the ionic conductivity of the suspension than through the movement of charged particles,[9] which reduces the deposition rate. The deposited layers show bad adherence to the substrate and are very inhomogeneous. By adding acid to the suspension, not only the pH-value is shifted, but also the conductivity is rising. Hence there is only a small pH-window where the suspension is stable ($\text{pH} < 6.2$) and the suspension conductivity still low enough ($\text{pH} > \sim 5.0$). Similar effects regarding not the pH-value but deflocculant content have been reported in.[10,11]

Not only conductivity affects deposition characteristics, but also a dependence of solids content can be observed. There is only a small range of solids content where significant EPD takes place. With solids contents below 4 vol% no applicable electrophoretic deposition of particles on the substrate can be achieved. With solids contents too high the higher viscosity of the suspension results in a superposed dip coating effect, which leads to an inhomogeneous coating and to a noticeably higher thickness in the trenches. With 8 vol% of solids content, thickness easily exceeds 10 µm. Additionally, the problem with too high electrical conductivity can exist, even though it was observed that with suspensions with higher solids content also higher conductivity is tolerable not to show the above mentioned negative effects on EPD. The conductivity correlated with pH-value and solids content can be seen in Figs. 6 and 7, respectively.

At a pH-value of about 5, being the lower limit of pH-value, the conductivity is above 200 µS/cm for 5 vol% suspensions and above 250 µS/cm for 6 vol% suspensions. Even though the EM is close to 3×10^{-8} m^2/V s in this pH-region (see Fig. 6), results show inhomogeneous deposition and striations across the substrate. At a pH-value above 6.2, the suspension being close to the isoelectric point (IEP) is unstable. The conductivity is between 130 and 150 µS/cm and the mobility is around 1×10^{-8} m^2/V s. According to HS this leads to a zeta-potential below 15 mV, which is considered to lead to unstable suspensions.[4] Best results have been achieved with 6 vol% suspension at pH-values in the range of 5.5–5.7, leading to conductivities of ca. 200 µs/cm. The EM in this pH-region is about 2×10^{-8} m^2/V s.

Fig. 7 illustrates that the conductivity depends almost linearly from the solids content. Supposedly, the powder

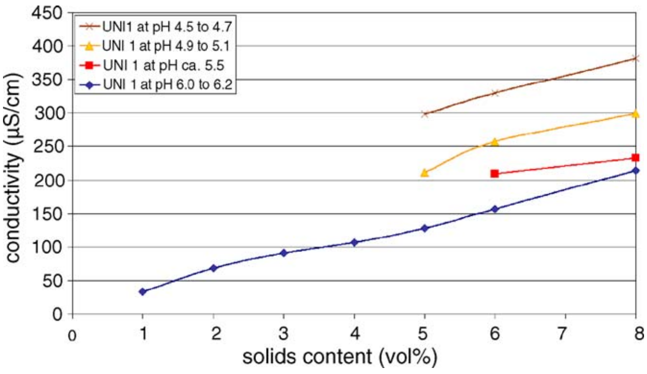

Fig. 7. Dependence of conductivity on solids content for UNI1 suspensions at different pH-values.

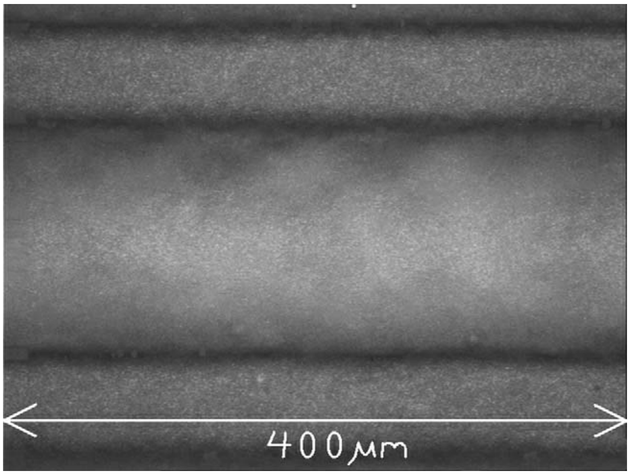

Fig. 8. Deposit of 6 vol% UNI1 suspension at pH-value 5.5, EPD for 5 s at −0.5 V.

possesses ionic contamination, which raises the conductivity of the suspension.

Two additional conductivity values were measured in alkaline medium (the two rightmost in Fig. 6) after adding 0.1 M tetra-methyl-ammonium-hydroxide (TMAH) instead of HCl for stabilization. However, EPD-experiments with alkaline suspensions (5 vol% solids content) did not lead to satisfying results, as the coatings were very inhomogeneous.

The thickness of a deposit attained at optimal suspension parameters is about 5 μm in the trenches and about 2 μm on the top of the profile, after depositing 5 s at −0.5 V potential (see Fig. 8).

Problems may occur during sintering of the substrates. Even though the nanoscaled ceramic particles show a high sintering activity,[13] the metallic steel substrate also is affected by the high temperatures. Sintering in oxygen containing atmosphere also leads to oxidation of the substrate. Therefore, inert gas atmosphere like argon gas is required to avoid oxidation.

Reasonable results could be achieved with rapid sintering at 1000 °C for 15 min (Figs. 9–11, SEM-pictures). The substrate is put into the heated furnace for 15 min (here with oxygen containing ambient gas atmosphere) and is then removed from the furnace to cool down to room temperature. Even though the thermal stress at these heating and cooling rates is rather high, the ceramic layer does not deform or delaminate from the substrate. Fig. 9 shows the sintered coating across the trenches. It is homogeneous and without cracks except for some minor local defects. However, a fully dense sintered layer cannot yet be achieved at these conditions. Fig. 10 shows the grain structure at higher resolution. A relatively high porosity still remains. Fig. 11 shows the cross-section of a sintered substrate. It can be seen that the ceramic layer has a thickness of about 5 μm, a homogeneous particle arrangement and levelling the roughness of the trenches' surface.

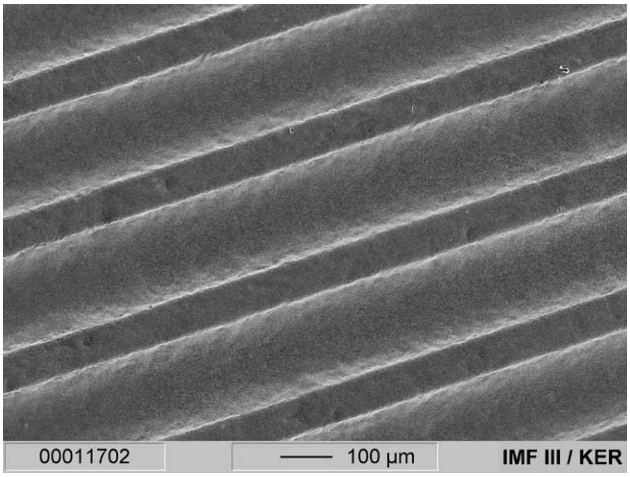

Fig. 9. Sintered substrate, 15 min at 1000 °C, top view.

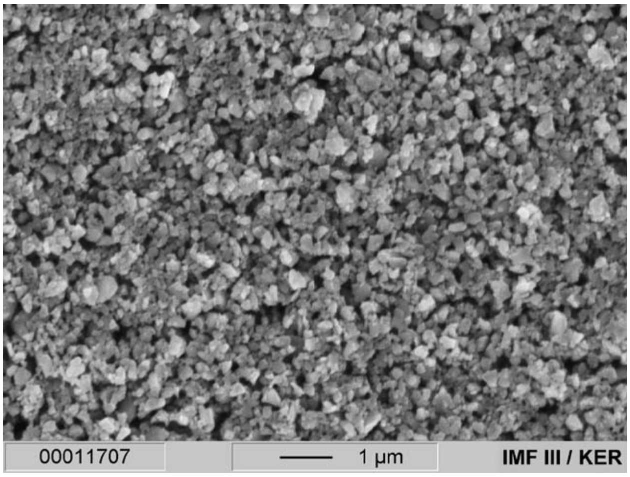

Fig. 10. Sintered particles on substrate.

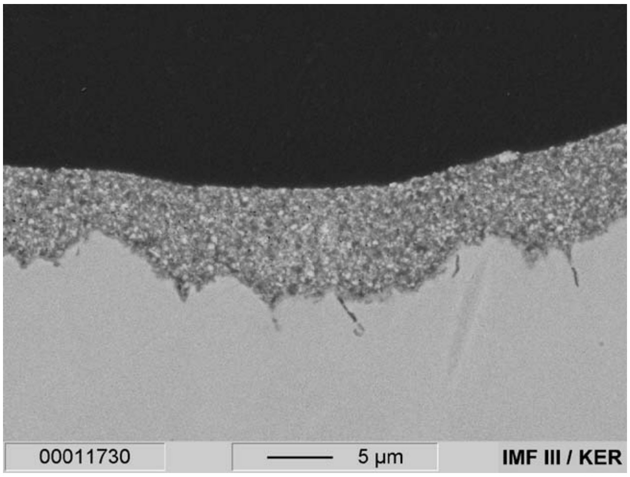

Fig. 11. Cross-section of the sintered substrate.

5. Summary

The intention of this work was to deposit thin zirconia ceramic layers on microstructured steel substrates. Therefore, suspensions with nanoscaled zirconia powders were used. By analyzing the electrokinetic behavior of nanoscaled zirconia particles, it could be shown that there is a dependence of particle size on electrophoretic mobility. If the zeta-potential of all particles, regardless of their size, is assumed to be constant, the mobility correlates with the term of the Henry function, where retardation and relaxation effects have to be taken into account.

The characterization of zeta-potential depending on pH-value is also important for the stability of suspensions. Experiments have shown that suspensions of the Unitec PYT05.0-001H zirconia powder in acidic media are only in a small pH-range suitable for deposition. At a pH-value of about 5.5, zirconia layers on microstructured steel substrates with a thickness of approximately 5 μm can be produced at a deposition time of 5 s at a potential of −0.5 V.

These layers are dried in vacuum and sintered at 1000 °C for 15 min. However, the sintered ceramic is not yet fully dense. To overcome this problem, the use of even finer particles would be helpful to achieve an even higher sinter activity. Another problem is the oxidation of the substrate at high temperatures under ambient gas atmosphere, though this can easily be prevented by sintering under an inert gas atmosphere (e.g. argon).

It could be shown, that the electrophoretic deposition of nanosized zirconia is possible. After sintering, homogeneous and crackfree layers on microstructured steel substrates can be produced. Therefore, this process seems to be a promising technique for the production of ceramic layers with a thickness of a few microns on microstructured surfaces.

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