

Influence of processing parameters on microstructure and ferroelectric properties of PZT-coated SiC fibers

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Abstract

SiC fibers have been coated with coprecipitated PZT powders by electrophoretic deposition. Zr and Ti hydroxides, respectively, and Pb carbonate are precipitated from homogenous nitrate solutions at pH values between 5 and 7. The platinum-coated SiC fibers were electrophoretically coated with these coprecipitated PZT powders after calcination and milling. The coated fibers were sintered at temperatures of about 1170 °C. With the low solid yield of the suspension and the low layer thickness compared to the sparking distance an almost constant growth rate of the layer is observed during electrophoretic deposition of the PZT powders at a coating voltage of 50 V and a coating time of up to 180 s. Remanence and coercive field strength characteristics of the fibers sintered at 1170 °C increase with increasing sintering time and density and range between 11 and 25 $\mu\text{C}/\text{cm}^2$, respectively, between 12 and 22 kV/cm in good correspondence with literature values for pure PZT fibers. © 2004 Elsevier Ltd. All rights reserved.

Keywords: Microstructure; Ferroelectric properties; Coatings; PZT coating; Fibers; SiC fibers

1. Introduction

A great field of potential applications has been opened up by ultrasonic and pyroelectric sensors, DRAMs, optoelectronic measuring systems as well as actuators with ferroelectric thin and thick film layers.^{1–4} Moreover, for some years piezoceramic tapes and fibers have been developed^{5,6} that are to take over both sensoric and actuatoric functions by utilizing the ferroelectric and the inverse ferroelectric effect.⁷ Ferroelectric fibers are produced by the so-called viscous solution spinning process,^{8,9} by extrusion of polymer/PZT blends^{10,11–13} or by the sol–gel technique.^{14–19} The great disadvantage of these piezo-fibers is their low stability under mechanical stress in use. The target of the presented studies was therefore to deposit PZT layers on SiC fibers by electrophoresis. It was expected that this method allows to produce fibers with a uniform layer thickness. On the other hand with a low cost equipment and a short process time a layer thickness can be expected which is significant higher than those achieved with CVD or PVD.^{20–23} When sintering PZT layers onto SiC fibers PbO may vaporize^{24–28} and chemical

reactions are to be expected in the boundary layer. Therefore the sintering temperature should be as low as possible. Extremely fine grained powders with low sintering temperatures may be achieved by precipitating metal hydroxides or oxalates from a metal salt solutions.^{29–35} Therefore in this paper coprecipitated PZT powders have been used which have been precipitated from homogeneous nitrate solutions.

2. Experimental details

2.1. SiC fiber

For the coating experiments the SiC fiber type SCS-6 SiC (Textron Special Team Materials, Lowell, MA, USA) was used. To prevent chemical reactions in the boundary layer between fiber and PZT layer the SiC fibers were coated with a platinum layer of 50 nm thickness (Laboratory Magnetron Sputtering Equipment, Type: LA 2503).

2.2. Powder preparation

To prepare a PZT powder by the coprecipitation process nitrates have been used as starting materials. $\text{Pb}(\text{NO}_3)_2$ and $\text{ZrO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ are commercially available (Riedel

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deHäen AG, Germany). An aqueous $\text{TiO}(\text{NO}_3)_2$ solution has been created from Titanyle sulphate $\text{TiO}(\text{SO}_4) \cdot x\text{H}_2\text{O}$ (Riedel deHäen AG, Germany) by dissolving it in distilled water and mixing the solution with NH_4OH . The purified $\text{TiO}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ was dissolved in concentrated 65% nitric acid (HNO_3 , Riedel deHäen AG, Germany) and so converted into $\text{TiO}(\text{NO}_3)_2$.

Nitrate solutions with the stoichiometric composition of $\text{Pb}:\text{Zr}:\text{Ti} = 1:0.52:0.48$ were mixed from individual solutions with concentrations of 0.01 to 0.1 mol%. The concentrations of the solutions were determined thermogravimetrically (STA 429, Netzsch, Germany). Because of the Pb vaporization during the sintering process for some samples an excessive PbO quantity of 15 mol% was added to the solutions. At pH values from 5 to 7 Zr and Ti nitrates may be precipitated as hydroxides, while Pb may be precipitated as carbonate. In order to precipitate the soluble Pb salt as PbCO_3 , urea ($\text{CO}(\text{NH}_2)_2$, Riedel de Häen AG, Germany) was added to the solution in a concentration of 0.1 to 1 mol% as titrating agent. Urea disintegrates in the temperature range above 100°C to create ammonium and cyanate ions.^{29,36,37} The final solutions were therefore stored in a closed receiver for 12 h at 120°C . The cyanate ion will create ammoniac and carbonate ions that enable PbCO_3 to precipitate. A detailed description of the coprecipitation process can be seen from.³⁸

The emerging product was filtered out by means of a glass filter pump and washed with distilled water thereafter. The gel-like filter cake was dried for 24 h at a temperature of 80°C . After calcination at temperatures between 650 and 750°C and 60 and 180 min the powder was ground by means of yttrium-stabilized ZrO_2 grinding balls (1 mm diameter) in an attritor with ethanol as dispersing agent.

2.3. Electrophoretic coating

For the electrophoretic coating process a mixture of distilled water, ethanol, acetone and acetylacetone was used as dispersing agent. Ethylene glycol was added to stabilize the slip. The solid yield of the suspension was 0.5 wt.%. The mixed solution was experimentally proved to be effective for control of the composition of deposited layers. The behavior of the powder in the solvent media is described in ref. 39.

Fig. 1 shows the schematic test set-up for the electrophoretic coating process. The distance between the SiC fiber and the counter-electrode was 20 mm. The varying parameters were current density, voltage and coating time. In order to avoid any sedimentation in the solution and concentration differences between the areas close and far to the electrodes the solution was stirred during electrophoretic coating. After the coating process the layer thickness was determined by means of a scanning electron microscope at 10 different points of the dried sample.

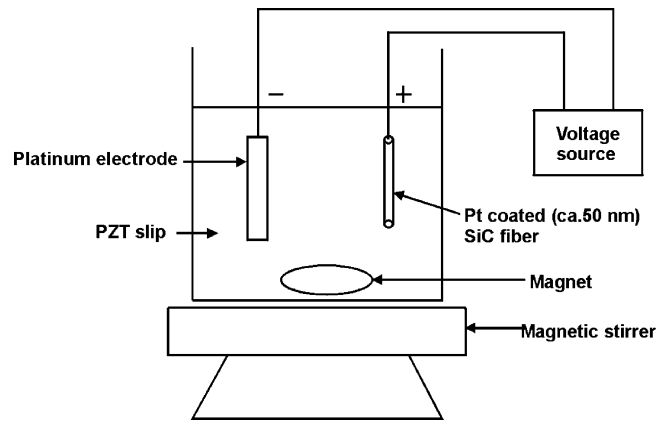


Fig. 1. Schematic view of the electrophoretic precipitation equipment.

2.4. Sintering experiments and microstructural characterization

The coated fibers were sintered in a PbO-enriched atmosphere created by a powder bed of $\text{PbZrO}_3 + 5 \text{ wt.}\% \text{ ZrO}_2$ in a platinum crucible. The samples were preheated in an oxidizing atmosphere at 700°C , followed by a heating rate of $10^\circ\text{C}/\text{min}$ to reach the final temperature of 1170°C . The thickness of the layer, the fracture surface and the surface of the sintered samples were examined by scanning electron microscopy (Cam Scan CS4, Cambridge, UK). The element distribution in the boundary layer between fiber and PZT layer was analyzed by EDX. (Tracor Northern TN 5502, USA). Mineral phases have been analyzed using XRD (Phillips, PW 1710).

2.5. Ferroelectric hysteresis

To measure the ferroelectric characteristics of the deposited PZT layer it was necessary to apply electrodes both on the SiC fibers and on the PZT layer (Fig. 2). This coating with metallic platinum was done in a vacuum sputtering equipment (Laboratory Magnetron Sputtering Equipment, LA 2503). The layer thickness of the platinum electrode was $<0.05 \mu\text{m}$. To achieve a uniform thickness the fiber was rotated during vaporization and the layer thickness was controlled by piezo-sonic sensors.

The hysteresis was measured at room temperature (Hewlett-Packard LCR Meter, type 4274). The sinusoidal electric signal used was created by a Hewlett Packard

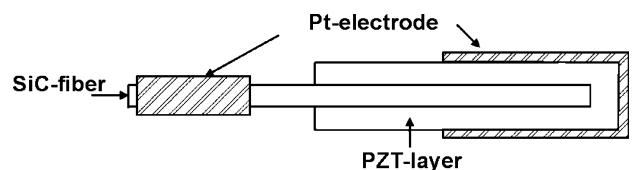


Fig. 2. Schematic view of the platinum electrodes on the PZT-coated SiC fiber.

Arbitrary Waveform Generator of 100 Hz frequency and a voltage of about 150 kV.

3. Results and discussion

3.1. Powder preparation

X-ray analysis shows that no other phase than hydrocerussite $[(\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2)\text{-phase}]$ and cerussite $[\text{Pb}(\text{CO}_3)\text{-phase}]$ appeared in the dried precipitation product (Figs. 3 and 4). Crystalline phases containing Zr or Ti ions did not appear. The intensity of the peaks of the hydro-cerussite phase decreases with increasing temperature. At temperatures of 290 °C and higher hydrocerussite has been transformed into cerussite. At temperatures of 320 °C PbO is formed from the cerussite phase because of decarbonization.

At 400 °C ZrO_2 and Ti_7O_{13} have been formed. At 620 °C PbZrO_3 can be observed. At 650 °C the phase conversion

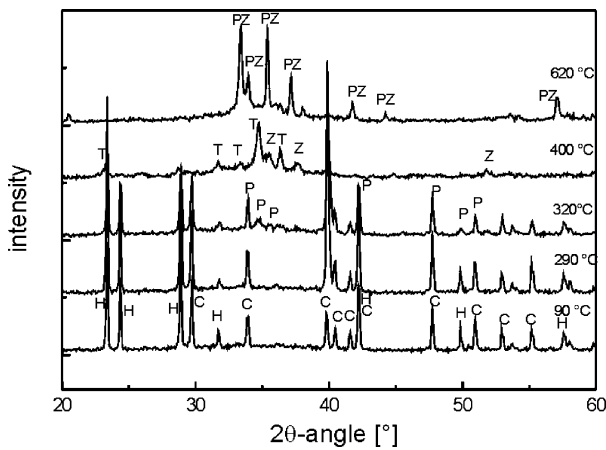


Fig. 3. X-ray diffraction data of powders heat treated at different temperatures. H: hydrocerussit; C: cerussit; Z: ZrO_2 ; T: Ti_7O_{13} ; PZ: PbZrO_3 ; P: PbO.

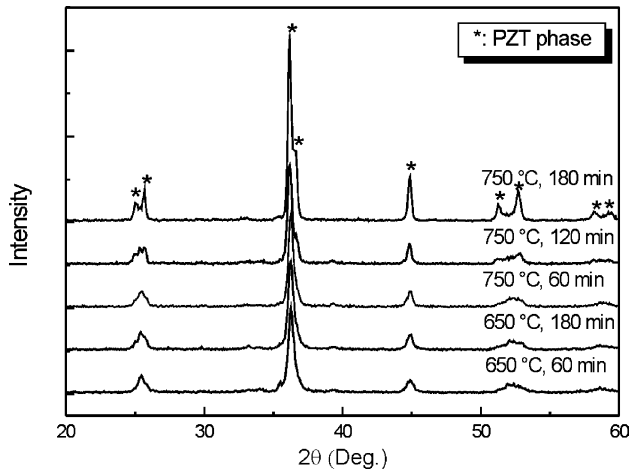


Fig. 4. X-ray diffraction data of powders heat treated at different temperatures and times.

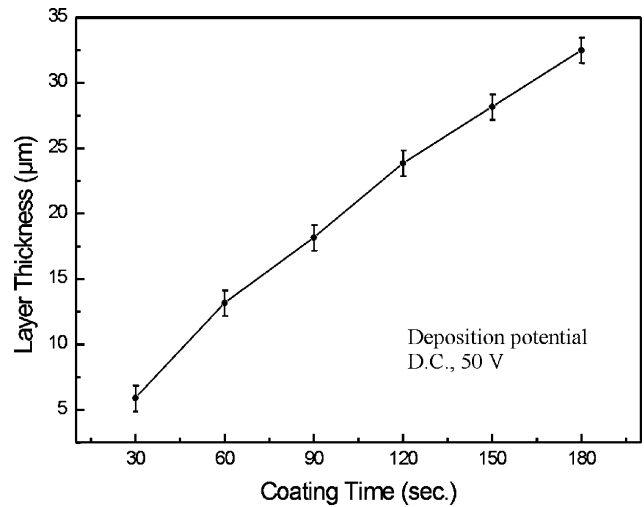


Fig. 5. Deposited layer thickness vs. coating time at constant deposition potential.

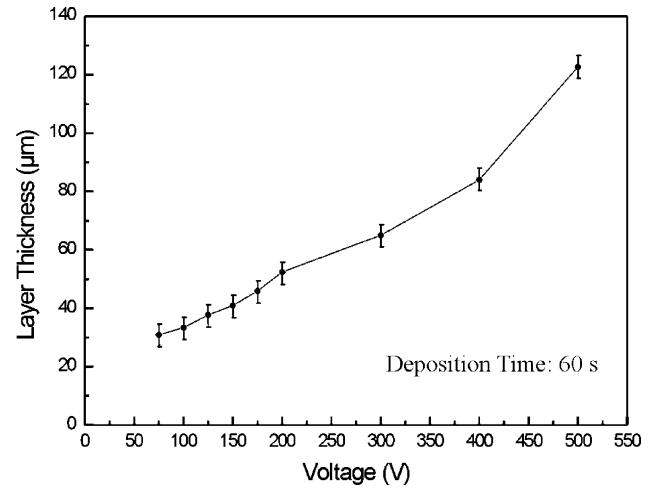


Fig. 6. Deposited layer thickness vs. applied voltage at constant deposition time.

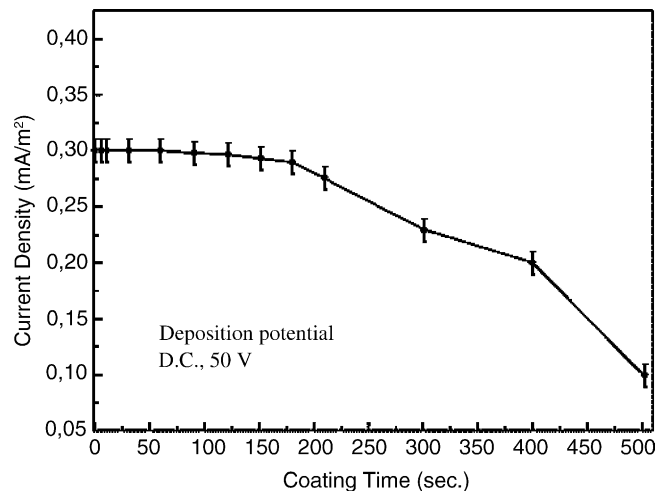


Fig. 7. Current density vs. coating time at constant deposition potential.

from PbO , ZrO_2 , Ti_7O_{13} and PbZrO_3 into the perovskite modification $\text{Pb}(\text{Zr,Ti})\text{O}_3$ has been found out for the first time (Fig. 4). The intensity of this perovskite phase grows by steady prolongation of the thermal treatment. A peak splitting was observed in the 2θ angle range between 24° and 26° for the powder that had been heat treated at

750°C for 120 min which has been described in ref. 40 too.

In this angle range the twin line of the tetragonale perovskite phase appears and additionally that of the rhombohedral phase of $(102)R$. The powders used for electrophoretic deposition were calcined at 750°C for 3 h and ground for

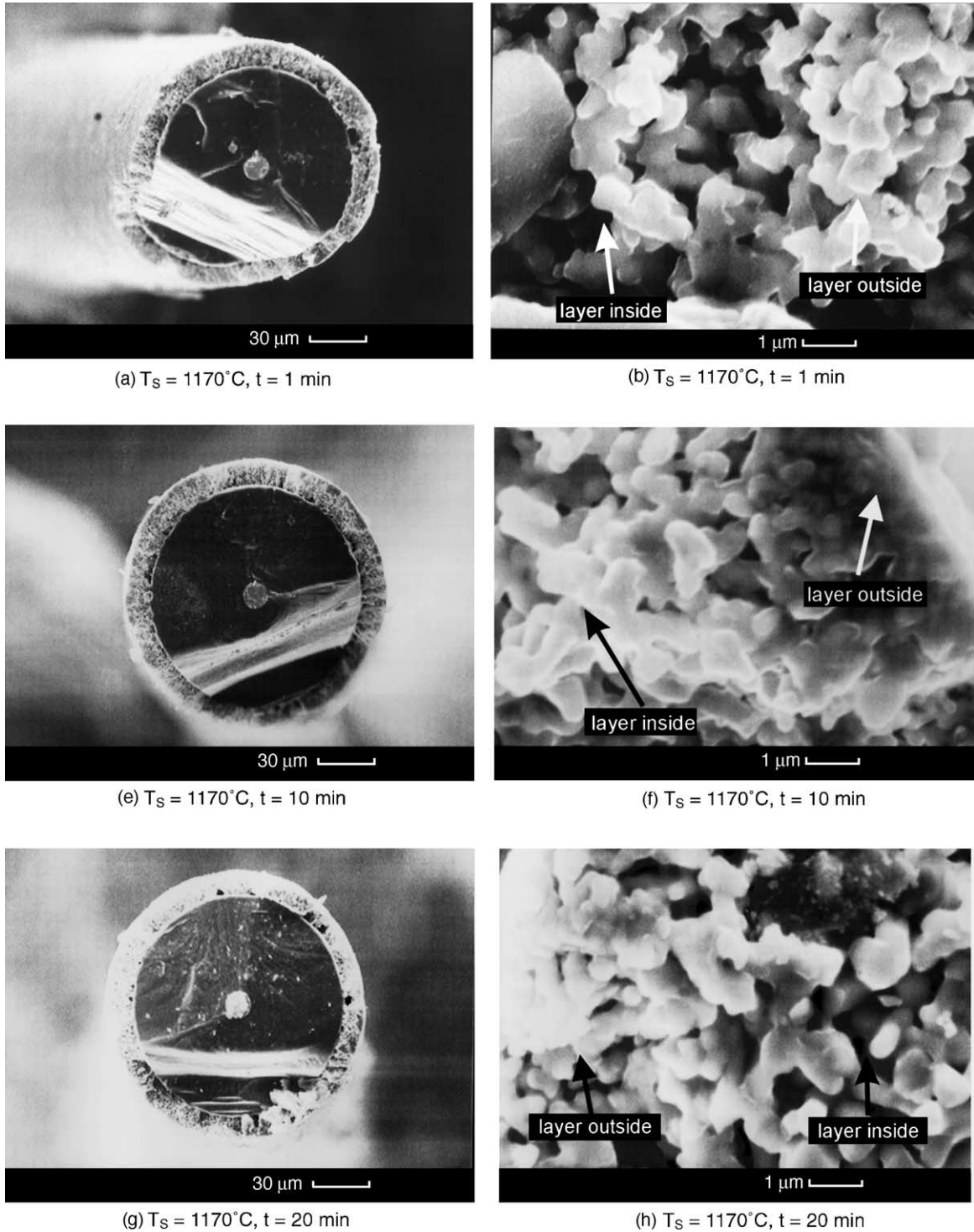


Fig. 8. Fracture surfaces of PZT-coated SiC fibers sintered at 1170°C at different holding times (SEM, BE).

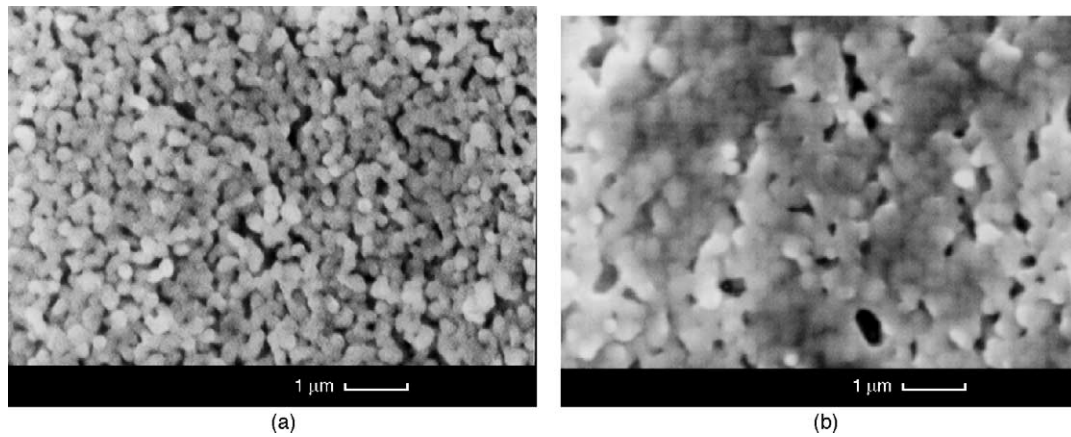


Fig. 9. Surface of PZT-coated SiC fibers sintered at 1170 °C at different holding times: (a) 1 min, (b) 10 min. Heating rate: 20 °C/min (REM).

540 min to a d_{50} of 0.51 μm and a corresponding specific surface area of 9.1 m^2/g .

3.2. Electrophoretic deposition

In this work the solid yield of the suspension is very low (0.5 wt.%), i.e. the major part of the dispersing agent is responsible for the electric conductivity. The specific conductivity of the deposited layer is much lower than the specific conductivity of the suspension. The thickness of the deposited layer on the other hand is very small compared to the distance of the electrodes ($d_S = 2 \text{ cm}$, $d_D \leq 50 \mu\text{m}$, see Appendix A) from which one may conclude that we may count on a linear time-controlled layer growth in the early stage of the electrophoretic deposition process as it had been actually observed in this study (Fig. 5).

In order to examine the effect of the deposition time on the layer thickness the fibers were coated at 50 V D.C. for a period of 30–180 s. The maximum layer thickness that could be achieved without cracking during drying of the coated fibers was about 40 μm .

When changing the electric voltage as coating variable the thickness of the deposited layer increases almost linear with increasing voltage (Fig. 6). Up to 500 V the layer thickness increases to about 120 μm . But as already mentioned above a thickness of about 40 μm the fibers could not be dried without creating microcracks in the deposited layer.

Fig. 7 shows the current density as function of the coating time under a constantly applied electric direct voltage of 50 V. The current density remains almost constant up to a coating time of 150 s and decreases with increasing coating time. The appearance of constant current density up to a

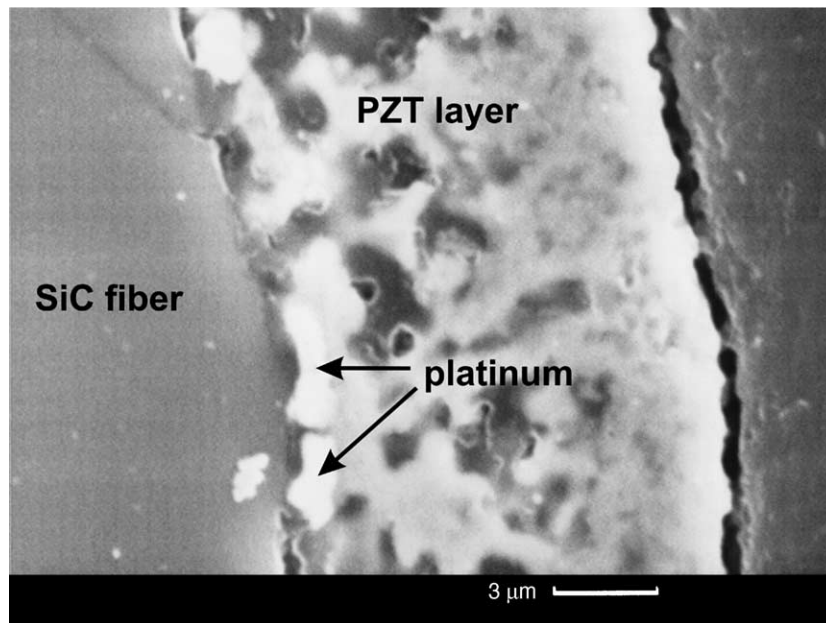


Fig. 10. Fracture surface of a PZT-coated SiC fiber with a platinum interlayer sintered at 1170 °C and a holding time of 20 min. Heating rate: 20 °C/min (REM).

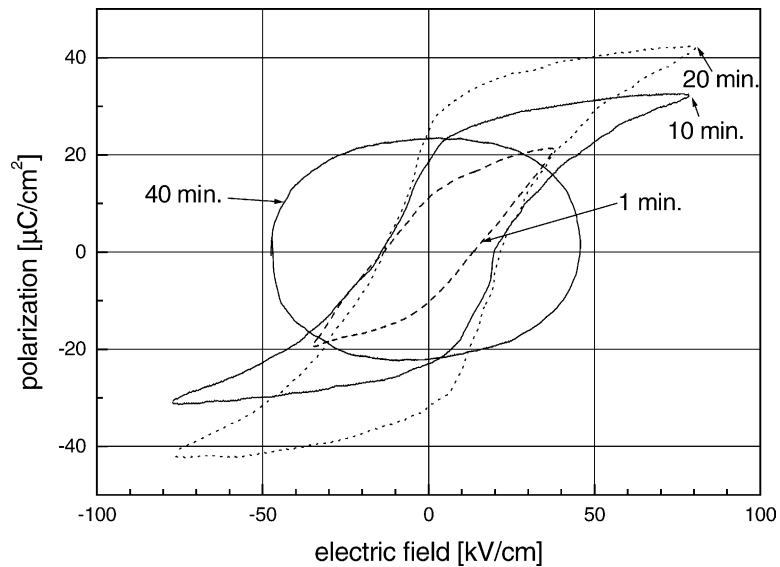


Fig. 11. Hysteresis curves of PZT-coated SiC fibers (50 V, 90 s). Sintering temperature: 1170 °C, holding time: 1–40 min.

period of 150 s is in accordance with the linear increase of the layer thickness in this period (Fig. 5). Above 150 s coating time both the conductivity of the solution and thus the current density decrease.

3.3. Sintering of PZT coatings on the fibers

SiC is thermodynamically unstable in oxidizing atmosphere at temperatures above 1000 °C and forms a thin SiO₂ layer on its surface. Smart and Glasser⁴¹ report that melting phases occur in the PbO–SiO₂ system in the range between 710 °C and 760 °C. Thus, for a PZT-coated SiC fiber the SiO₂ layer that normally protects against further oxidation will be destroyed which leads to further oxidation, respectively, to the formation of glassy phases. This has been observed for all sintering temperatures at low heating rates without platinum coating. With platinum-coated SiC fibers the formation of reaction zones could be drastically reduced.

Fig. 8 shows fracture surfaces of fibers that had first been coated with platinum and then with PZT powder under an electric direct voltage of 50 V and for a coating time of 90 s. They had been sintered at 1170 °C for a period of 1–20 min. X-ray diffraction examinations show exclusively PZT phases on the coated surface. The densification increases with increasing holding time (Figs. 9 and 10). After 20 min however the platinum interface starts to dissolve (Fig. 10). At longer holding times the Pt-layers began heavily to react with PZT.

3.4. Ferroelectric properties

Fig. 11 shows hysteresis curves measured on PZT layers deposited on SiC fibers at 50 V for a period of 90 s. The sintering temperature was 1170 °C, the holding times varied between 1 and 40 min. The fibers sintered at 1170 °C for 1–20 min show a typical hysteresis behavior.

With increasing holding time the remanence increases from 11.12 μC/cm² (1 min) to 24.92 μC/cm² (20 min), the coercive field strength increases from 12.32 kV/cm (1 min) to 21.52 kV/cm (20 min) which can be explained by the increased densification of the PZT layer. The ferroelectric characteristics correspond to the values described by Yoshikawa¹⁵ and Hong⁴² for PZT fibers. For the sample sintered for 40 min no hysteresis could be observed because of the fact that the intermediate platinum layer reacts with PZT to glassy phases.

4. Conclusion

PZT powders produced by coprecipitation, calcination and milling are very reactive and can be sintered on Pt-coated SiC fibers at 1170 °C between 1 and 20 min. At longer holding times PZT, Pt and SiC react to glassy phases. The suspensions used within the frame of this study have a low solid yield and the deposited layer thicknesses are small compared to the distance between the two electrodes used for electrophoretic deposition. The resulting linear layer growth could be proved by a mathematical model calculation. Layer thicknesses of about 40 μm could be achieved without cracking which is significant higher than those achieved by CVD or PVD. When determining the samples' polarization behavior in the electric field a hysteresis flow comes up that is typical for ferroelectrics. The ferroelectric characteristics remanence and coercive field strength increase with increasing densification of the PZT layer and are comparable to data for PZT fibers in the literature.

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Appendix A

Due to the voltage applied in the deposition process and due to the difference in the electropotential the particles migrate towards the substrate and separate there (Fig. 12).

Regarding the system of the electrophoresis equipment as a quantity of resistors connected in series in a circuit the equation of the electric parameters will be as follows:⁴³

$$\vec{J} = CuE = nze_0uE = nze_0u \frac{U}{d}, \tag{1}$$

where \vec{J} is the mass flow, C the solid yield of the suspension, u the mobility of the particles, E the field strength, n the number of charge carriers, z the electrochemical valency number, e_0 the unit charge, U the electric voltage and d the distance between the plates.

In steady-state operation the mass flows \vec{J}_S in the suspension and \vec{J}_D in the deposited layer are equal.

$$\vec{J} = \vec{J}_S = \vec{J}_D \tag{2}$$

In the suspension applies

$$\vec{J}_S = n_Sze_0u_S \frac{U_S}{d_S} = \frac{U_S}{R_S}, \tag{3}$$

where R_S is the electric resistance of the suspension.

In the deposited layer:

$$\vec{J}_D = n_Dze_0u_D \frac{U_D}{d_D} = \frac{U_D}{R_D}, \tag{4}$$

where R_D is the electric resistance of the deposited layer.

With applied electric direct voltage is

$$U_{total} = U_D + U_S \tag{5}$$

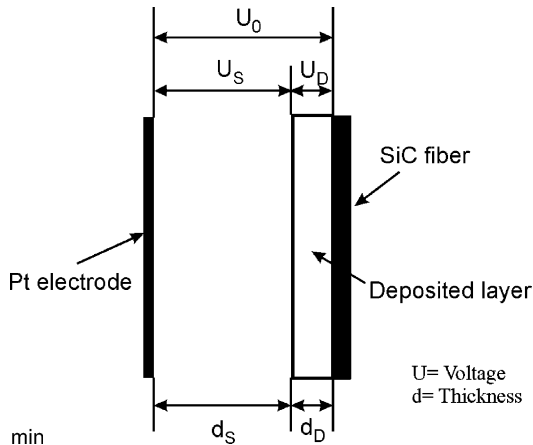


Fig. 12. Model used for calculating the thickness of the electrophoretically deposited PZT layer.

and

$$R_{total} = R_D + R_S \tag{6}$$

$$\vec{J}_{total} = \frac{U_{total}}{R_{total}} = \frac{U_{total}}{R_D + R_S}. \tag{7}$$

By inserting Eqs. (3) and (4) in Eq. (7) the result is as follows:

$$\begin{aligned} \vec{J}_{total} &= \frac{U_{total}}{(d_D/n_Dze_0u_S) + (d_S/n_Sze_0u_S)} \\ &= \frac{U_{total}}{(d_D/\tau_D) + (d_S/\tau_S)} \end{aligned} \tag{8}$$

where τ_D resp. τ_S designate the specific conductivity of the deposited layer, respectively, of the suspension ($\tau = n_i ze_0 u_i$).

The deposited mass m is indicated by integration of Eq. (8):

$$m = \int_0^t \vec{J}_{total} dt \tag{9}$$

The effectively precipitated layer thickness is indicated by Eq. (10):

$$d_D = \frac{m}{\rho} = \int \frac{\vec{J}_{total}}{\rho} dt \tag{10}$$

i.e. d_D is a function of time ($d_D(t)$), ρ is the density of the deposited layer.

By inserting Eq. (10) in Eq. (8) the result obtained for the deposition rate is (differential notation):

$$\frac{dx}{dt} = \frac{\vec{J}_{total}}{\rho} = \frac{U_{total}}{(x/\tau_D) + (d_S/\tau_S)} \frac{1}{\rho},$$

where $x = d_D$.

By integral calculus, it may be circumscribed as follows:

$$\int dx = \int \frac{U_{total}}{A + Bx} dt \text{ or} \tag{12}$$

$$\int A dx + \int Bx dx = \int U_{total} dx \tag{13}$$

where $A = (d_S/\tau_S)\rho$ and $B = (1/\tau_D)\rho$

By path integration it may now be converted into the following quadratic equation:

$$x^2 + 2 \frac{A}{B} x - \frac{U_{total}}{B} t = x^2 + 2K_1 x - K_2 t = 0 \tag{14}$$

with $K_1 = A/B$ and $K_2 = U_{total}/B$

By resolving this equation you get the following variation of the layer thickness.

$$x = -K_1 + \sqrt{K_1^2 + K_2 t} \tag{15}$$

$$x = - \left(\frac{\tau_D d_S}{\tau_S} \right) + \sqrt{\left(\frac{\tau_D d_S}{\tau_S} \right)^2 + \left(\frac{\tau_D U_{total}}{\rho} \right) t} \tag{16}$$

By resolving Eq. (16) the following two border conditions arise:

$$\frac{d_S}{\tau_S} \gg \frac{d_D}{\tau_D}$$

$$\frac{d_S}{\tau_S} \ll \frac{d_D}{\tau_D}$$

Is Eq. (12) resolved by the first condition, the layer thickness as a function of deposition time may be described as follows:

$$x = \frac{\tau_S}{d_S} t \quad (17)$$

Is Eq. (12) resolved by the second condition, the layer thickness as a function of deposition time may be described as follows:

$$x = \sqrt{2u\tau_S t} \quad (18)$$

References

- Yi, G., Wu, Z. and Sayer, M., Preparation of Pb(Zr,Ti)O₃ thin films by sol gel processing: Electrical, optical, and electro-optic properties. *J. Appl. Phys.* 1988, **64**, 2717–2724.
- Takayama, R. and Tomita, Y., Preparation of epitaxial Pb(Zr_xTi_{1-x})O₃ thin films and their crystallographic, pyroelectric, and ferroelectric properties. *J. Appl. Phys.* 1989, **65**, 1666–1670.
- Hagood, N. W. and von Flotow, A., Damping of structural vibrations with piezoelectric materials and passive electrical networks. *J. Sound Vib.* 1991, **146**, 243–268.
- Park, J. W., Recent technology trend of DRAM semiconductor device. *J. Korean Inst. Electric. Electron. Mater. Eng.* 1994, **7**, 157–164 (in Korean).
- Watzka, W. and Sporn, D., Composites with integrated piezoelectric ceramic fibers (in German). In *Verbundwerkstoffe und Werkstoffverbunde*, ed. K. Schulte and K. U. Kainer. Wiley-VCH, Weinheim, Germany, 1999, pp. 649–654.
- Beckert, W. and Kreher, W. S., Modelling of the effective properties of composites with piezoelectric fibers (in German). In *Verbundwerkstoffe und Werkstoffverbunde*, ed. K. Schulte and K. U. Kainer. Wiley-VCH, Weinheim, Germany, 1999, pp. 570–575.
- Sporn, D. and Schönecker, A., Composites with piezoelectric thin fibers—first evidence of piezoelectric behavior. *Mater. Res. Innovat.* 1999, **2**, 303–308.
- Cass, R. B., Fabrication of continuous ceramic fiber by the viscous suspension spinning process. *Am. Ceram. Soc. Bull.* 1991, **70**, 424–429.
- French, J. D. and Cass, R. B., Developing innovative ceramic fibers. *Am. Ceram. Soc. Bull.* 1998, **77**, 61–65.
- Cai, S., Miller, C. E., Pedersen, L., Sørensen, O. T. and Xu, Y., Extrusion and properties of lead zirconate titanate piezoelectric ceramics. *Ferroelectrics* 1997, **196**, 69–72.
- Gururaja, T. R., Schulze, W. A., Shrout, T. R., Safari, A., Webster, L. and Cross, L. E., High frequency application of PZT/polymer composite materials. *Ferroelectrics* 1981, **39**, 1245–1248.
- Waller, D. J., Safari, A., Card, R. and Toole, M. O., PZT fiber/polymer composites prepared by a replication process. *J. Am. Ceram. Soc.* 1990, **73**, 3503–3506.
- Janas, V. F. and Safari, A., Overview of fine scale piezoelectric ceramic/polymer composite processing. *J. Am. Ceram. Soc.* 1995, **78**, 2946–2955.
- Meyer, Jr. R., Lead zirconate titanate fine fibers derived from alkoxide-based sol-gel technology. *J. Am. Ceram. Soc.* 1998, **81**, 861–868.
- Yoshikawa, S., Pb(Zr,Ti)O₃ (PZT) fibers—fabrication and measurement methods. *J. Int. Mater. Sys. Struct.* 1995, **6**, 152–158.
- Chewasatn, S. and Milne, S., Sol-gel synthesis and characterization of PbTiO₃ fibres. In *Proc. 3rd Eur. Ceram. Soc. Conf.* Madrid, Spain, Faenca Editrice Iberica SA, 1993, pp. 335–340.
- Aoki, S. I., Choi, S. C., Payne, D. A. and Yanagida, H., Sol-gel processing of PbTiO₃ ceramic fibers. *Mater. Res. Soc. Symp. Proc.* 1990, **180**, 485–490.
- Seth, V. K. and Schulze, W. A., Fabrication and characterization of ferroelectric PLZT 7/35/65 ceramic thin films and fibers. *Ferroelectrics* 1990, **112**, 283–307.
- Sporn, D., Watzka, W., Schönecker, A. and Pannkoke, K., Smart structures by integration of piezoelectric PZT fibers—present state and future applications. *Adv. Sci. Technol.* 1999, **25**, 279–286.
- Arato, T., Narisawa, T., Koganesawa, N. and Nonaka, Y., Forming of alumina insulation layers by double step electrophoretic deposition. *J. Ceram. Soc. Jpn.* 1992, **100**, 75–79.
- Zhitomirsky, I., Electrophoretic and electrolytic deposition of ceramic coatings on carbon fibers. *J. Eur. Ceram. Soc.* 1998, **18**, 849–856.
- Sweeny, T. G. and Whatmore, R. W., Electrophoretic deposition of ferroelectric thin films. *Ferroelectrics* 1996, **187**, 57–73.
- Tassel, J. V. and Randall, C. A., Electrophoretic deposition and sintering of thin/thick PZT films. *J. Eur. Ceram. Soc.* 1999, **19**, 955–958.
- Tandon, R. P., Singh, V. and Singh, R., Properties of low temperature sintered neodymium doped lead zirconate titanate ceramics. *J. Mater. Sci. Lett.* 1994, **13**, 810–812.
- Wittmer, D. E. and Buchanan, R. C., Low temperature densification of lead zirconate-titanate with vanadium pentoxide additive. *J. Am. Ceram. Soc.* 1981, **64**, 485–490.
- Ohtaka, O., Von Der Mühl, R. and Ravez, J., Low-temperature sintering of Pb(Zr,Ti)O₃ Ceramics with the aid of oxyfluoride additive: X-ray diffraction and dielectric studies. *J. Am. Ceram. Soc.* 1995, **78**, 805–808.
- Faber, M., Langguth, J. and Greil, P., Preparation and characterization of PZT submicron powders using a spray-pyrolysis process. *Ceram. Trans.* 1995, **51**, 63–67.
- Patel, N. D. and Nicholson, P. S., Comparison of piezoelectric properties of hot-pressed and sintered PZT. *Am. Ceram. Soc. Bull.* 1986, **65**, 783–787.
- Matijević, E., Monodispersed metal (hydrous) oxides—a fascinating field of colloid science. *Acc. Chem. Res.* 1981, **14**, 22–29.
- Sugimoto, T., Preparation of monodispersed colloidal particles. *Adv. Colloid Interface Sci.* 1987, **28**, 65–108.
- Rhine, W. E., Saegusa, K., Hallock, R. B. and Cima, M. J., Control of ceramic powder composition by precipitation techniques. *Ceram. Trans.* 1990, **12**, 107–118.
- Matijević, E., Preparation of monodispersed ceramic powders by precipitation from homogeneous solutions. In *Powder Processing Science. Proc. 2nd Int. Conf.* Berchtesgaden, German Ceramic Society, 1989, pp. 25–34.
- Karakas, Y. and Lee, W. E., Processing and phase evolution in ZnO varistor prepared by oxide coprecipitation. *Br. Ceram. Trans.* 1994, **93**, 65–70.
- McNamara, V. M., A wet chemical method for the preparation of oxide mixtures applicable to electronic ceramics. *J. Can. Ceram. Soc.* 1965, **34**, 103–120.
- Akbas, M. A. and Lee, W. E., Characterisation and densification of PLZT powder coprecipitated from chloride-nitrate solutions. *Br. Ceram. Trans.* 1996, **95**, 49–52.
- Dixit, M., Subbanna, G. N. and Kamath, P. V., Homogeneous precipitation from solution by urea hydrolysis: a novel chemical route to the β-hydroxides of nickel and cobalt. *J. Mater. Chem.* 1996, **6**, 1429–1432.

37. Akinc, M., Jongen, N., Lemaitre, J. and Hofmann, H., Synthesis of nickel hydroxide powders by urea decomposition. *J. Eur. Ceram. Soc.* 1998, **18**, 1559–1564.
38. Kim, J.-W., *Electrophoretic Coating of SiC Fibers with Coprecipitated PZT-Powders*. Ph.D. thesis, Technical University Clausthal, Germany, 2001.
39. Yamashita, K., Nagai, M. and Umegaki, T., Fabrication of green films of single- and multicomponent ceramic composites by electrophoretic deposition technique. *J. Mater. Sci.* 1997, **32**, 6661–6664.
40. Cheon, C.-I. and Kim, H.-G., Effects of chemical inhomogeneity on phase coexistence in $\text{Pb}(\text{Zr,Ti})\text{O}_3$ ceramics at morphotropic tetragonal and rhombohedral phase boundary. *J. Korean Ceram. Soc.* 1990, **27**, 1027–1033.
41. Smart, R. M. and Glasser, F. P., Compound formation and phase equilibrium in the system PbO-SiO_2 . *J. Am. Ceram. Soc.* 1974, **57**, 378–382.
42. Hong, G.-G., *Preparation of Fine Powders of the System $\text{Al}_2\text{O}_3/\text{ZrO}_2$ by Precipitation Method and Properties of Its Sintered Ceramics*. Ph.D. thesis, Yon Sei University, Korea, 1989.
43. Kingery, W. D., Bowen, H. K. and Uhlmann, D. R., *Introduction to Ceramics*. John Wiley & Sons, New York, Chichester, Brisbane, Toronto, Singapore, 1975.