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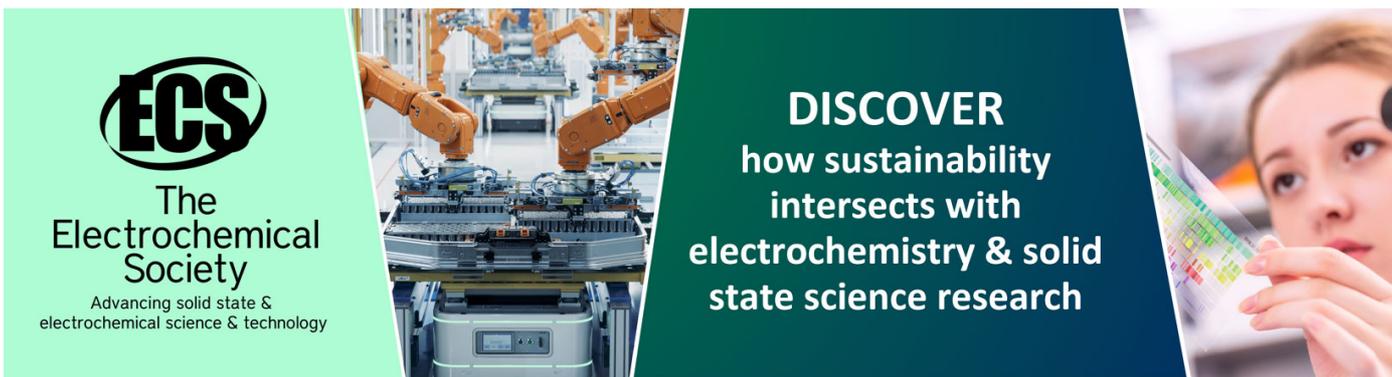
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# Structured ceramic surfaces by preceramic polymer demixing processes

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**Abstract.** Polymeric and ceramic coatings with a cellular structure have been manufactured based on demixing processes by the use of two different preceramic polymers and silicon carbide fillers in a dip coating process. The rheological properties of the coating system were adjusted by adding a monomeric silane and methanol, and the crosslinking process was triggered by the addition of catalysts. The surface tension of the coating system was measured and a temperature range for coating and structure formation was identified. The as coated substrates were investigated with respect to an influence of the substrate microstructure and the coating speed on the cellular structure of the coatings. While the substrate microstructure has no influence on the cell structure the coating speed led to a minor change in the cell width. The as received thermoset coatings were pyrolyzed and the structure was intact even after firing at 1100 °C in different atmospheres.

## 1. Introduction

To make a material suitable for specific applications, coating of the materials' surface may be a possible way. Coatings may provide protection against corrosion, oxidation, abrasion, or they may provide an additional functionality to the material. To generate ceramic coatings, numerous established processes such as atmospheric plasma spraying, electron-beam physical vapor deposition, RF sputtering or chemical vapor deposition can be applied [1].

A novel route for material coating makes use of preceramic polymers. Preceramic polymers can be processed via cost efficient polymer manufacturing routes in connection with low-temperature conversion into a ceramic material, which is called a polymer derived ceramic (PDC) [2]. An overview of this processing route is given in [3]. The processing scheme of PDCs includes the steps mixing/dissolving in a solvent, introduction of particulate fillers (optional), shaping and thermal conversion. The fillers such as alumina, silica, nonoxide ceramic powders, metal or intermetallic powders may be used to adjust the coating properties, and they may behave inert showing no reaction with the preceramic polymer at elevated temperatures, or they may react and are addressed as active fillers. An overview of this matter is given in [4].

PDC coatings can be applied by cost efficient processes like spray, dip or rotational coating. In the past years the feasibility was demonstrated, and different types of PDC coatings on metal or ceramic



substrates were generated. Relevant work was published in [5-10], and the applications are in the field of corrosion protection, oxidation protection and abrasion protection. A similar processing route was applied to generate structured coatings based on demixing processes within a coating slurry during coating or dewetting processes of the coating system on the substrate surface [11, 12]. The principle of structure formation in the aforementioned work is based on the use of two different preceramic polymers which are not miscible to each other. They are dissolved in a solvent which guarantees dissolubility of both components, and while the solvent evaporates, a demixing process of the two polymers start and leaves behind a net-like structure with cells in the range of some tens of micrometers. Details are given in [12].

In this work the influence of the substrate's microstructure on the net-like structure of the polymer coating was investigated. Rheological properties, wettability of an alumina substrate, surface tension and surface energy of the system are discussed. The preservation of the structure after pyrolytic conversion into a PDC material is demonstrated.

## 2. Experimental

### 2.1 Processing

The coatings were produced by a dip-coating process on an alumina substrate with a filler-loaded slurry containing two preceramic polymers. The preceramic polymers were 9.2 vol.% polymethylphenylvinylsiloxane (PMPS, Silres H62C,  $[(C_6H_5)_{0.44}(CH_3)_{0.24}(C_2H_3)_{0.16}H_{0.16}SiO_{1.5}]_n$ ) and 9.2 vol.% polymethylsiloxane (PMS, Silres MK,  $[CH_3SiO_{1.5}]_n$ , both Wacker Chemie GmbH, Munich, Germany). As solvents 8.1 vol.% methyltriethoxysilane (MTES,  $[(C_2H_5O)_3SiCH_3]$ , Wacker Chemie GmbH, Munich, Germany) and 53.8 vol.% methanol (MeOH, ROTIPURAN®  $\geq 99.9\%$ ,  $[CH_3OH]$  Carl Roth GmbH + Co. KG, Karlsruhe, Germany) were used. To crosslink the preceramic polymers 1.1 vol.% oleic acid ( $C_{18}H_{34}O_2$ ) and 0.6 vol.% aluminium acetylacetonate ( $C_{15}H_{21}AlO_6$ , both from Merck KGaA, Darmstadt, Germany) were used. The filler material was 18.1 vol.% silicon carbide (SiC, SM07,  $d_{50}$  1.3–1.7  $\mu m$ , ESK-SiC GmbH, Frechen, Germany).

The first step of slurry manufacturing was to dissolve the PMPS in MTES while stirring with a magnetic stirrer. After ten minutes of stirring PMS was added slowly in small portions. To guarantee a homogeneous solution stirring was continued for two more hours. Methanol was introduced into the mixture and after another 30 minutes of stirring the SiC filler material was added. Finally the catalysts were introduced into the slurry after another stirring for 15 minutes. To guarantee homogeneity of the slurry it was stirred for 18 more hours.

As substrate material  $Al_2O_3$  tapes (Keral96, KERAFOL Keramische Folien GmbH, Eschenbach, Germany) were used for the surface coating. In order to support our hypothesis that microstructure, i. e. the grain size of the substrate material might influence the cellular surface structure of the preceramic polymer coating resulting from demixing/dewetting the alumina tapes were heat treated to trigger grain growth. Heat treatment was carried out in a chamber furnace at 1600 °C for 4, 8, 16 and 24 hours, and grain sizes were measured to range from 2.5  $\mu m$  before thermal treatment to  $\sim 5 \mu m$  after 24 hours of firing.

In order to get information about the slurry – substrate interaction, the contact angles between the slurry and the alumina tapes were measured with an OCA20 + SCA22, DataPhysics Instruments GmbH, Filderstadt, Germany. From the results the surface tension of the preceramic slurry was calculated. Therefore a 0.8 mm or a 1.2 mm canula was used to inject the slurry to the measurement chamber. The measurements were performed in a methanol saturated atmosphere and in normal atmosphere (air) in a temperature range from 20 °C to 50 °C. To have a comparison with other materials, the surface tension of water, diiodomethane and ethylene glycol was measured on the  $Al_2O_3$  substrate.

Coating was carried out with a self-constructed dip coater. The withdrawal speed was adjusted to 10 mm  $s^{-1}$  and to 20 mm  $s^{-1}$  and the hold time in the slurry before withdrawal was 10 seconds. To obtain a thermoset surface layer after dip coating the samples were dried for 24 hours at room

temperature and crosslinked for 24 hours at 110 °C in a drying furnace (ED 53, Binder GmbH, Tuttlingen, Germany). Selected samples were pyrolyzed in argon atmosphere, in nitrogen atmosphere or in air at 1,100 °C. The heating rate was 5 K min<sup>-1</sup> and the dwell time at peak temperature was 4 hours.

## 2.2 Sample characterization

The cellular structure of the coatings was characterized using a scanning electron microscope (XL30 ESEM-FEG, FEI, Eindhoven, Netherlands). The Al<sub>2</sub>O<sub>3</sub> tapes coated with the preceramic polymer/SiC-slurry were sputtered with gold and SEM images were recorded with the same magnification (2,000 x) for all samples in order to compare the structures. The height/depth of the demixing structures was analyzed with a 3D microscope (InfiniteFocus, Alicona GmbH, Schönau, G.).

Crystallographic phase identification was performed with X-ray diffraction analysis with an Empyrean diffraction analysis system (PANalytical, Kassel-Waldau, Germany). The coatings were investigated by the grazing incidence method using monochromated CuK<sub>α</sub> radiation, and the peak identification was carried out by the search-match algorithm using the powder diffraction file (PDF) database.

## 3. Results and Discussion

### 3.1 Surface tension, contact angle and wettability

With the OCA system the contact angle of water, ethylene glycol and diiodomethane on heat-treated (0 h - 24 h at 1600 °C) Al<sub>2</sub>O<sub>3</sub> tapes was measured in air. The contact angle in the initial state of water and ethylene glycol was very high, indicating a low surface tension. The polar part of the surface tension was low. From these findings we deduced that a coating process with a polar coating system leads to partial dewetting of the slurry from the substrate material, and a coating process might not be possible.

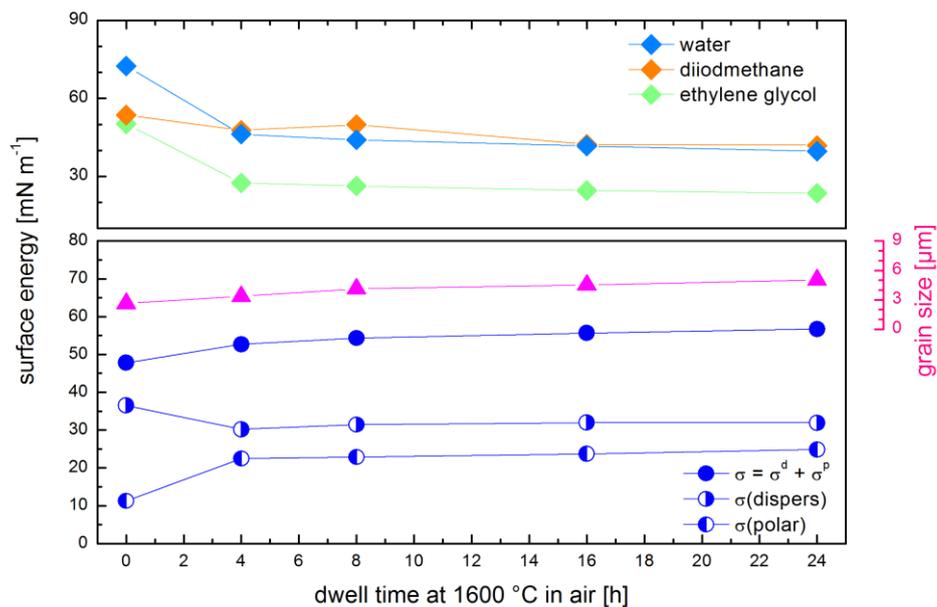


Fig. 1 Surface properties as a function of the heat treatment process of the alumina substrates as a function of firing time.

After the heat treatment of the alumina substrates the contact angle of water and ethylene glycol decreased; the surface tension and its polar component increased deducing the coating with a polar system might be possible. The contact angle of diodemethane did not change significantly, thus the change of the surface properties is mainly influenced by the polar characteristics of the substrate. No influence of the duration of the heat treatment, i. e. the grain growth (2  $\mu\text{m}$  to 5  $\mu\text{m}$ ) on the surface tension was observed as can be seen in Fig. 1. On the heat treated tapes the wettability of the slurry was measured, and there was no significant influence of the tapes' microstructure.

The surface tension was also measured with the OCA system in the temperature range from 20 °C to 50 °C in air. In this experiment two different surrounding atmospheres were used for comparison: one set of experiments was performed in the presence of methanol in the atmosphere within the measuring chamber and the other set of experiments was performed without methanol in the measuring atmosphere. In this experiment air was the surrounding medium. The contact angles were measured first using water, ethylene glycol and diodemethane, and at least the contact angle of the SiC containing coating system was measured. Based on these data the surface tension was calculated by the OWRK method [13-15]. Fig. 2 shows the change of the contact angle with the increase of the temperature. In both sets of experiments (air and methanol containing atmosphere) an increase of the contact angle with increasing temperature was measured. This behavior was found for water, diode methane and ethylene glycol as well as for the preceramic slurry. In air as surrounding atmosphere, the contact angle of water increased in the temperature range from 20 °C to 50 °C from 70 ° to 80 °, of ethylene glycol from 36 ° to 40 ° and from diodemethane from 50 ° to 53 °. The contact angle of the preceramic slurry showed an increase from ~35 ° to ~45 °, and a decrease of the surface tension by approximately 4  $\text{mN m}^{-1}$  was found ranging from 42  $\text{mN m}^{-1}$  at 20 °C to 38  $\text{mN m}^{-1}$  at 50 °C. While the disperse part was constant (not shown in the diagram), the polar part decreased by 8  $\text{mN m}^{-1}$  to ~5  $\text{mN m}^{-1}$ . This indicates a deterioration of the coating performance of the preceramic polymer system with increasing temperature. In fact, in supplementary experiments a change in the coating behavior was found showing no structure formation after coating at temperatures higher than 30 °C. Besides the surface tension the evaporation of methanol at elevated temperatures might influence the phase separation process and thus the structure formation. Methanol is a necessary component for the formation of the net-like structures.

Methanol as surrounding atmosphere has a significant influence on the surface tension of the diode methane and on the preceramic slurry. The contact angle of diodemethane increased from 59 ° to 61 ° in methanol atmosphere and is significantly higher in comparison to that in air (50 ° to 53 °). A minor change was observed for the contact angle of ethylene glycol in methanol, which lies between 40 ° and 41 °, while that in air is in the range between 36 ° and 40 °. The contact angle of water did not show any change by the change of atmosphere. The contact angle of the preceramic slurry showed an extension of its values in methanol: in air it was between 35 ° and 45 ° and in methanol it is between 32 ° and 54 ° in the temperature range from 20 °C and 50 °C.

The surface tension decreased from 38  $\text{mN m}^{-1}$  to 35  $\text{mN m}^{-1}$  in the methanol loaded atmosphere, showing a decrease of the disperse part from 33  $\text{mN m}^{-1}$  to 28  $\text{mN m}^{-1}$  while the polar part was almost constant. This means that the wettability changes with an increase of the temperature, which is mainly attributed to the nonpolar part. From these findings we deduced that the structure formation changes with the change of the coating atmosphere, and in methanol as the surrounding atmosphere also no demixing structures were formed at temperatures higher than 25 °C

### 3.2 Cellular structure of the coatings

Fig. 3 shows the cellular/net-like structure on the heat-treated  $\text{Al}_2\text{O}_3$  tapes (heat treatment from 0 h to 24 h at 1600 °C) after coating with different withdrawal speeds (0  $\text{mm s}^{-1}$  and 20  $\text{mm s}^{-1}$ ).

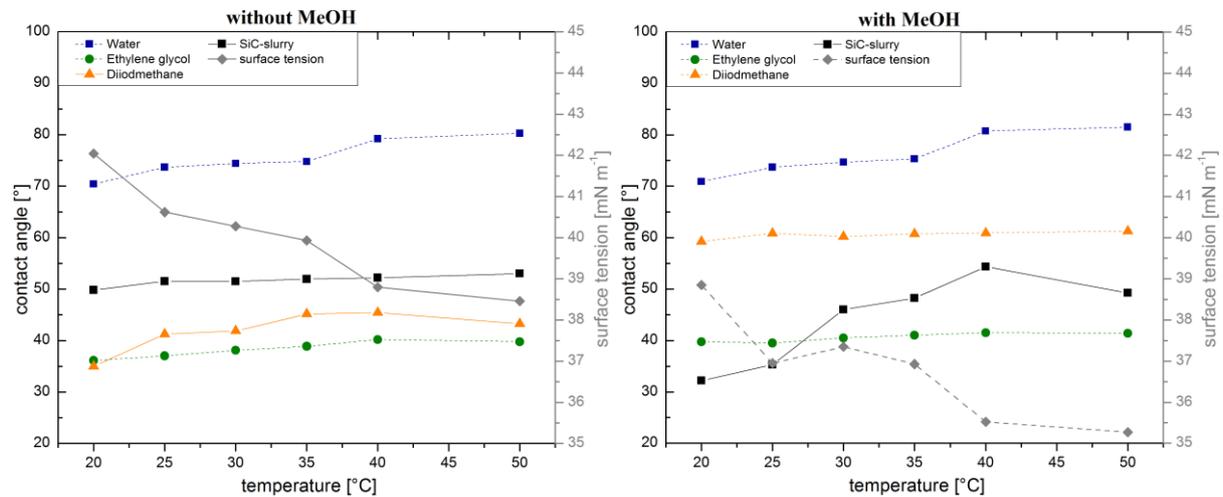


Fig. 2 Contact angle and surface tension of the preceramic slurry on the  $\text{Al}_2\text{O}_3$  substrate at different temperature; left: experiment in air as surrounding atmosphere; right: experiment in methanol saturated atmosphere.

No influence of the heat treatment and thus of the grain size of the substrate material was found. The change in the coating speed indicated only a minor influence on the net-like structures: With a coating speed of  $10 \text{ mm s}^{-1}$  the cell width of the net-like structures were  $6.5 \mu\text{m} - 7.2 \mu\text{m}$  and with a coating speed of  $20 \text{ mm s}^{-1}$  the cell width slightly increased having a value of  $7.5 \mu\text{m} - 8.4 \mu\text{m}$ .

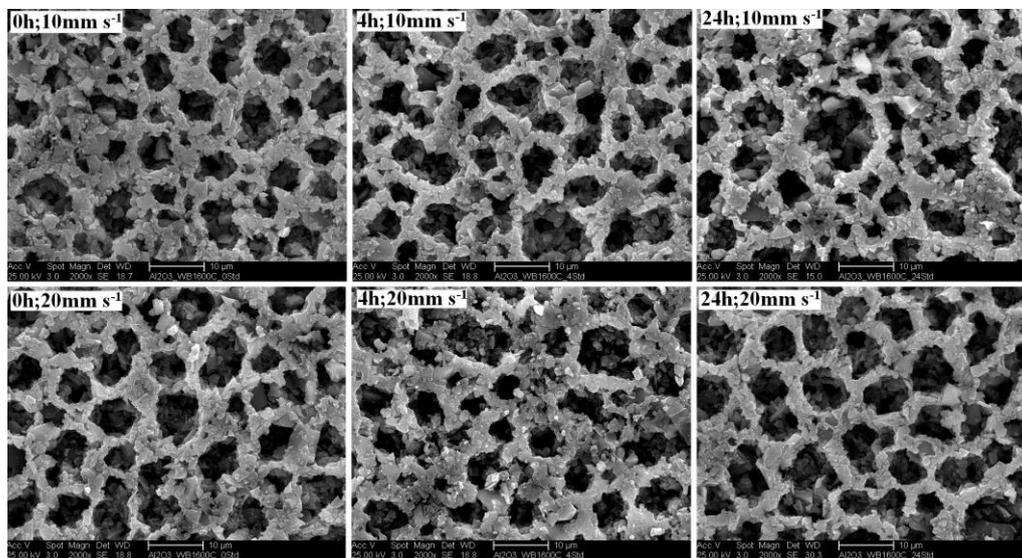


Fig. 3 SEM images of the coated alumina substrate; top (coating speed:  $10 \text{ mm s}^{-1}$ ): left: substrate as purchased; middle: substrate fired for 4 h at  $1600 \text{ }^\circ\text{C}$ ; right: substrate fired for 16 h at  $1600 \text{ }^\circ\text{C}$ ; bottom (coating speed:  $20 \text{ mm s}^{-1}$ ): left: substrate as purchased; middle: substrate fired for 4 h at  $1600 \text{ }^\circ\text{C}$ ; right: substrate fired for 16 h at  $1600 \text{ }^\circ\text{C}$ .

Fig. 4 shows the height profiles of the coated tapes for samples coated with a speed of  $10 \text{ mm s}^{-1}$  and fired for the as purchased sample and two samples fired for 4 h and 24 h, respectively, as a false color image. The depth scale ranges from  $+10 \mu\text{m}$  (red) to  $-10 \mu\text{m}$  (blue). No difference was observed

in the cell depth as a function of the heat treatment of the alumina substrate. Also the coating speed has no influence on the cell depth (not shown). The maximum depth was measured to range between -6  $\mu\text{m}$  and -8  $\mu\text{m}$ .

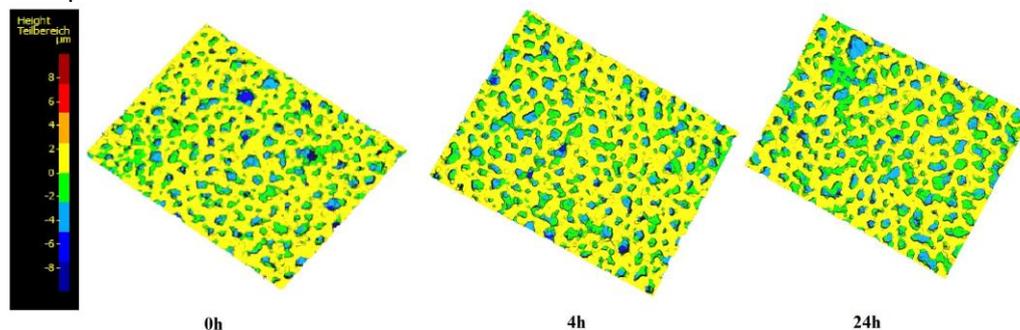


Fig. 4 Height profiles of coated alumina tapes (coating speed of  $10 \text{ mm s}^{-1}$ ); left: coating on a tape as purchased; middle: coating on a tape which was fired for 4 h at  $1600 \text{ }^\circ\text{C}$ ; right: coating on a tape which was fired for 24 h at  $1600 \text{ }^\circ\text{C}$ .

### 3.3 Microstructure of the coatings

Fig. 5 shows the results of the X-ray diffraction analysis. The coated tapes were crosslinked and fired at different conditions: in air, in nitrogen or in argon at  $1100 \text{ }^\circ\text{C}$ . From XRD measurements can be seen, that the firing atmosphere does not have any influence on the microstructure of the coating on the tapes at this temperature. No differences were found in the XRD spectra, and the crystalline phases have been identified to be silicon carbide. There is no hint to the formation of a crystalline silica or carbon phases. Pyrolysis at higher temperatures, however, may result in the formation of cristobalite, graphite and a second generation of silicon carbide, which result from the transformation of the preceramic polymer.

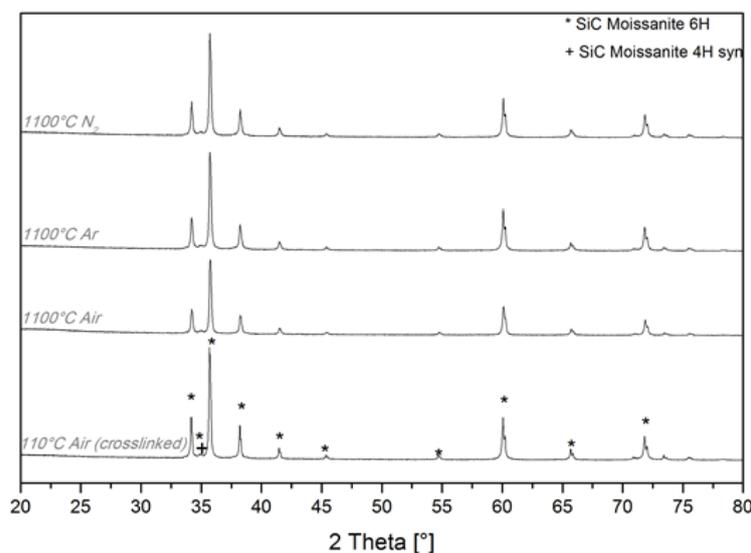


Fig. 5 XRD spectra of the preceramic polymer slurry coated tapes after pyrolysis in air, in nitrogen or in argon at  $1100 \text{ }^\circ\text{C}$ .

## 4. Conclusions

In this work a SiC filled preceramic slurry was used for dip coating of as purchased and as fired alumina tapes. Firing of tapes was applied to vary the grain size of the tapes used for coating.

The slurry and the tapes were characterized by an optical analysis system to measure the contact angle between the slurry and the tape, and the surface tension in the temperature range between 20 °C and 50 °C and in air or in methanol as surrounding atmosphere. Dip coating of the tapes was carried out with two different coating speeds and the resulting cellular structure was characterized with SEM while the microstructure was analyzed after firing at 1100 °C by means of x-ray diffraction.

A temperature increase lead to a decrease in the surface tension of the preceramic slurry resulting in a deterioration of the coating performance of the slurry, and coating temperatures of > 30 °C did not result in the formation of cellular structures on the alumina tapes. The variation in grain size of the substrate did not show any influence on the cellular structure of the coatings. The cell width was only influenced by the coating speed.

Firing of the as-coated substrates resulted in a shape retention of the cellular structure, and microstructure analysis indicated the formation of a ceramic coating after firing. This coating method can be applied to generate cellular demixing structures from preceramic polymers, and it might be the only method to produce ceramic demixing structures.

## References

- [1] Scheffler F, Torrey J.D., in: P. Colombo, G.D. Soraru, R. Riedel, A. Kleebe (Eds.), *Polymer Derived Ceramics: Theory and Applications* (Hardcover), DESTech Publications Inc., Lancaster, PA, USA, 2009
- [2] Greil P, Active-Filler-Controlled Pyrolysis of Preceramic Polymers *J. Am. Ceram. Soc.* 1995 **78** 835
- [3] Colombo P, Mera G, Riedel R., Soraru G D ,Polymer-Derived Ceramics: 40 Years of Research and Innovation in Advanced Ceramics *J. Am. Ceram. Soc.* 2012 **93** 1805
- [4] Polymer derived ceramics, P. Colombo G.D. Soraru R. Riedel A. Kleebe (Eds.), DESTech Publications, 2009, ISBN 978-1-605-95000-6
- [5] Günthner M, Kraus T, Krenkel W, Motz G, Particle-Filled PHPS Silazane-Based Coatings on Steel *Int J Appl Ceram Technol* 2009 **6** 373
- [6] Günthner M, Schütz A, Glatzel U, Wang K, Bordia R K, Greißl O, Krenkel W, Motz G, High performance environmental barrier coatings, Part I: Passive filler loaded SiCN system for steel *J Eur Ceram Soc* 2011 **31** 3003
- [7] Günthner M, Schütz A, Glatzel U, Wang K, Bordia R K, Greißl O, Krenkel W, Motz G, High performance environmental barrier coatings, Part II: Active filler loaded SiOC system for superalloys *J Eur Ceram Soc* 2011 **31** 3011
- [8] Kappa M, Kebainyor A, Scheffler M, A two-component preceramic polymer system for structured coatings on metals *Thin Solids Films* 2010 **519** 301
- [9] Torrey J D, Bordia R K, Henager C, Blum Y, Shin Y, Samuels W D, Composite polymer derived ceramic system for oxidizing Environments *J Mater Sci* 2006 **41** 4617
- [10] Torrey J D. Bordia R K, Phase and microstructural evolution in polymer-derived composite systems and coatings *J. Mater. Res.* 2007 **22** 1959
- [11] Stern E, Heyder M, Scheffler F. Micropatterned Ceramic Surfaces by Coating with Filled Preceramic Polymers *J Am Ceram Soc* 2009 **92** 2438
- [12] Woiton M, Heyder M, Laskowsky A, Stern E, Scheffler M, Brabec CJ Self-assembled microstructured polymeric and ceramic surfaces *J Eur Ceram Soc* 2011 **31** 1803
- [13] Kaelble D, Dispersion polar surface tension properties of organic solids *J. Adhes.* 1970 **2** 66
- [14] Owens D K and Wendt R C Estimation of the Surface Free Energy of Polymers *J. Appl. Polym. Sci.* 1969 **13** 1741
- [15] Rabel W, Einige Aspekte der Benetzungstheorie und ihre Anwendung auf die Untersuchung und Veränderung der Oberflächeneigenschaften von Polymeren *Farben und Lacke* 1971 **77** 997