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Ceramic coatings processed by spraying of siloxane precursors (polymer-spraying)

O. Goerke[a], E. Feike[a], T. Heine[a], A. Trampert[b], H. Schubert[a,*]

[a]Technische Universität Berlin, Institut für Werkstoffwissenschaften und technologien, Englische Strasse 20, 10587 Berlin, Germany
[b]Paul Drude Institut für Festkörperelektronik, Hausvogteiplatz 5–7, 10117 Berlin, Germany

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Abstract

Si-based inorganic polymers (siloxanes, silazanes, carbosilanes, etc.) dissolved in an organic solution exhibit a sufficiently low viscosity to be processed by spraying. For this work methyl-silesquisiloxanes precursors have been used aiming for an Si–O–C composition. A two-flux nozzle has been designed and build-up which enables a full beam of about 12° opening angle. The primary particle size of the sprayed droplet was in the range of 5–10 μm. If the substrate is sufficiently near to the nozzle the droplets could wet and coat the surface. High temperature treatment under flowing nitrogen initiated a polymerisation (200 °C) followed by ceramisation at higher temperatures (up to 1000 °C). In spite of the weight loss, a good bonding of the coating on the substrate without delamination or segmentation cracks was obtained, which could be demonstrated by SEM and TEM investigations. The shrinkage was anisotropic and occurred predominantly toward the surface rather than parallel. This type of thin film effect limited to a thickness to 3 μm/per coating cycle. The microstructure consisted out of an amorphous Si–O–C matrix with very small C precipitates. The interface is basically straight with an atomic bonding showing very good adhesion but also some adaptation dislocations on the substrate side.

Keywords: Coatings; Polymer spraying; Precursors-organic; Si–O–C; Surfaces

1. Introduction

Inorganic Si-based polymers (silanes, siloxanes, silazanes, carbosilanes, etc.) are subject of constant research.[1,2] These precursors have a polymer constitution in which the desired covalent bonds are already persisting in the as synthesised state and remain in the system through the total process.[3–5] The polymer processing has the advantage to avoid any type of powder and their associated problems like agglomerates, particle packing, heterogeneities and high sinter temperatures. Basically Si-polymers are thermoset-materials which start with a comparably short chain precursor and than undergo a network formation either due to heating, radiation or catalysis.[6–8] The material is then no longer meltable or soluble but it is still a polymer. A pyrolysis changes the entire molecular structure due to a loss of side groups which leaves an amorphous inorganic glassy material behind.

In this work the liquid status of the precursors was exploited for a spray atomisation process. Provided the viscosity of the precursor or solution is low enough a simple two flux nozzle can be used to produce a straight spray beam of fine droplets, which then coats the surface. The further process, however, requires a thermal treatment to reach a polymerisation (formation of 3D network) and ceramisation (loss of the polymer character, removal of side groups, formation of an inorganic glass) at elevated temperatures.[9–11] From the chemical engineering point of view there is a strong analogy to a thermoset polymer varnish (such as epoxy resins, polyurethane...), but with the addition of a pyrolysis.

The process was developed on the basis of siloxanes because of their easy handling in air without gas protection. The development of an appropiate nozzle, coating apparatus as well as thermal treatment followed by microstructural characterisation of coatings will be presented.

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* Corresponding author. Tel.: +49-30-314-24325; fax: +49-30-314-21100.
E-mail address: schubert@ms.tu-berlin.de (H. Schubert).

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2. Experimental

The precursors were chosen with respect to their solubility, their ceramic yield and the handling condition as well as the price (type H62C, Wacker-Chemie GmbH; type NH2100, Hüls Silicone GmbH; type 3PM2 and 3MO1, ABCR GmbH). They were dissolved in MPA [(1-methoxy-2-propyl)-acetate]. For atomisation two-flux nozzles with a 1-mm central pipe and a gas pressure setting of 2 bar were used.[12] Additionally the nozzle could heat electrically up to 200 °C in order to establish a fast solvent evaporation.[13] To achieve a homogenous thickness of the coating *x–y* and *z* movement as well as all the flux parameters had to be controlled, which was realised by a computer controller (LabView programm, Isel step motors, FieldPoint controller, electro-pneumatic valves). The movement of the substrate is 300 mm × 300 mm (Fig. 1).

The chosen precursors can be handled at room temperature without hydrolysis or oxidation. On further processing at elevated temperature the coatings were annealed in flowing nitrogen within alumina sealed tube furnace (Linn Hightherm). The pyrolysis process was monitored by a thermo balance (Netzsch STA 429) while the out-gasing reaction products where guided through a constantly heated (200 °C) teflon pipe to a gas cell. The detection was done by a FTIR spectrometer (Brüker Equinox 55, Germany).

The quality of the pyrolised coating was tested mainly by using Si-substrates because Si does not show mode in the IR spectrum. Since silicon wafers do not show IR absorption the coating could be inspected by FTIR without any further preparation.

The microstructure was investigated by SEM (Philips XL 20, The Netherlands) on fractured cross section as well as on as sprayed or as pyrolised specimens, respectively.

Surface roughness measurements were performed by the stylus method (Hommel Tester T2000).

For TEM inspection the material were prepared by diamond tools in cross section technique. The raw samples were polished dimple ground and finally ion milled (Gatan). The TEM investigation were carried out using a Jeol 1030 TEM with 300 kV acceleration voltage and a LaB_6 cathode.

3. Results and discussion

The spray process of polymeric precursors requires a sufficiently low viscosity of the polymer solution or of a polymer melt. First, melting was investigated because no additional solvent would be required in this process. According to the chemistry of the current precursor temperatures of more than 120 °C had to be achieved in order to decrease the viscosity below 100 mPa s for a uniform atomisation. However, in all cases the polymerisation had started already in this temperature regime and caused a rapid increase of the viscosity. Thus, all further experiments were carried out using organic solvents.

Due to the low viscosity of the precursor solutions, a two-flux nozzle has been used at a gas pressure of 2 bar. The small spray nozzle produces a symmetrical full cone spray pattern, almost round in coverage, and completely filled with fine drops. A typical spray cone is shown in Fig. 1b. The deposition rate is highest in the

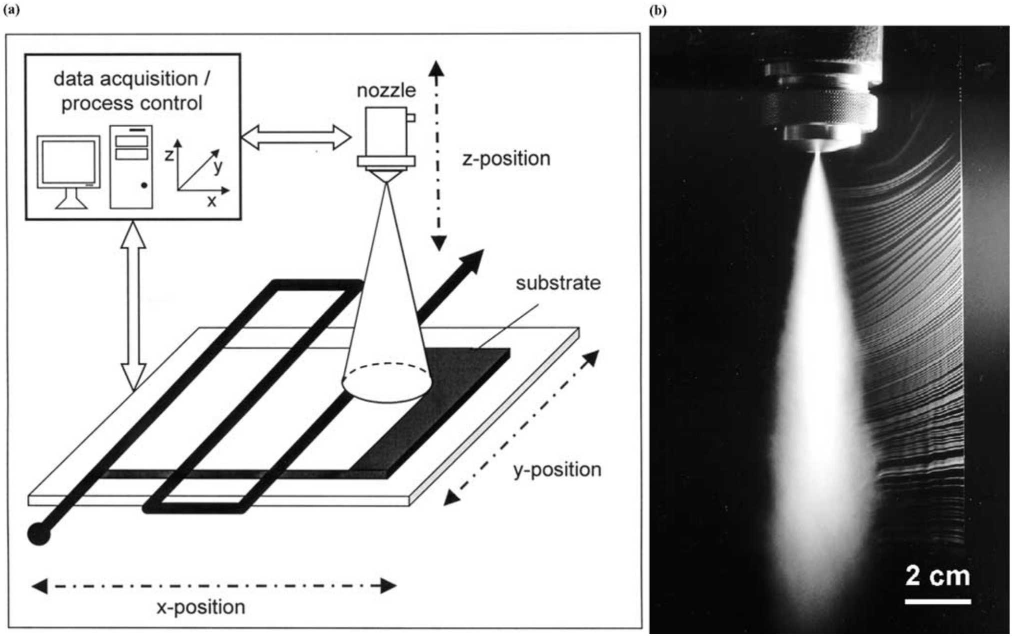


Fig. 1. Schematic diagram/configuration of the spray coater components (a) and the image of the spray cone (b).

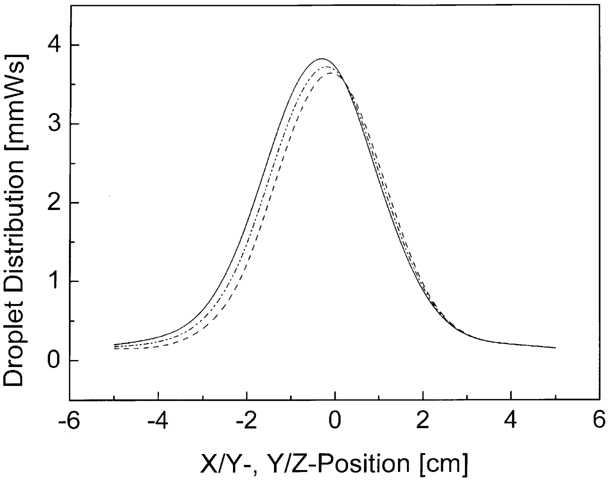


Fig. 2. Droplet distribution during spray-deposition.

axis of the nozzle (Fig. 2) forming a Gaussian distribution. Further, the particles in the middle are the fasted and had the highest temperature, again both in a Gaussian distribution.

The working distance for this type of nozzle was less than 300 mm. For longer distances the loss of solvent was high enough to create solid particles prior to hitting the surface. Fig. 3a and b shows a SEM micrograph and a particle size distribution. The particles have a primary droplet size of about 2–5 µm, which later formed agglomerates of about 10–20 µm in size.

3.1. Solvent removal and adhesion

It can be assumed that droplets of the polymer solution hit the substrate with a partly reduced content of solvent, because of the rapid evaporation during spraying. This effect helps to minimise the shrinkage on subsequent pyrolysis. If the target was additionally heated to about 150 °C the solvent removal occurred already during the coating process. The contact of the coating could be retained through the whole process. As a general tendency, a good wetting behaviour of the polymer solution on the substrate was necessary to achieve a continuous coating, which was observed for a medium polarity of the surface. The surface roughness was a second influence on the adhesion. A continuous coating layer could be established retained in the range from very smooth surfaces up to about 10 µm depth of roughness which corresponds to the size of a primary droplet. If larger surface pores were present, they typically lead to voids.

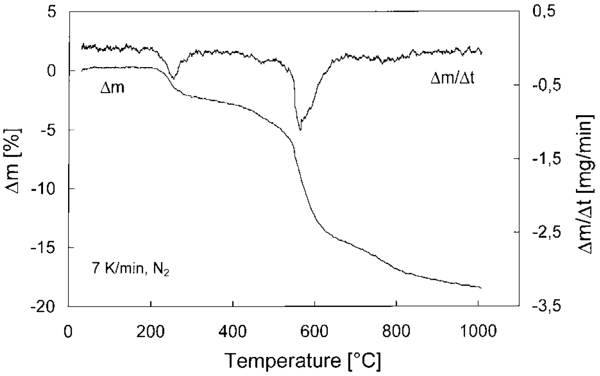


Fig. 4. TG curve of a poly(phenyl-methyl) silsesquioxane.

3.2. Polymerisation and pyrolysis

The pyrolysis of the sprayed coating occurred on a substrate, which is a strain-hindered situation. Thus, the removal of excess constituents of the material proceeds from the substrate interface through the coating toward the surface.[14–17] Fig. 4 shows a typical TG curve for a poly(phenyl-methyl)silsesquioxane with characteristic bimodal decomposition. In addition a thermo balance monitored the pyrolysis with an attached FTIR gas-analyser. The gas analysis showed that the first mass loss is preferably attributed to the removal of hydroxyl groups whereas the second part is mainly due to CH_x,

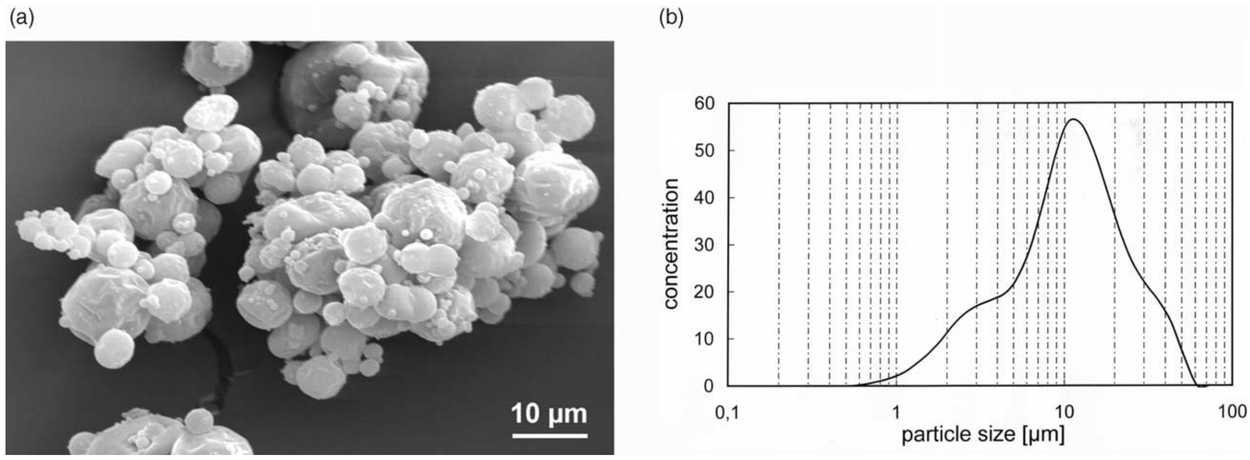


Fig. 3. SEM images of the sprayed particles (a) and the distribution (b).

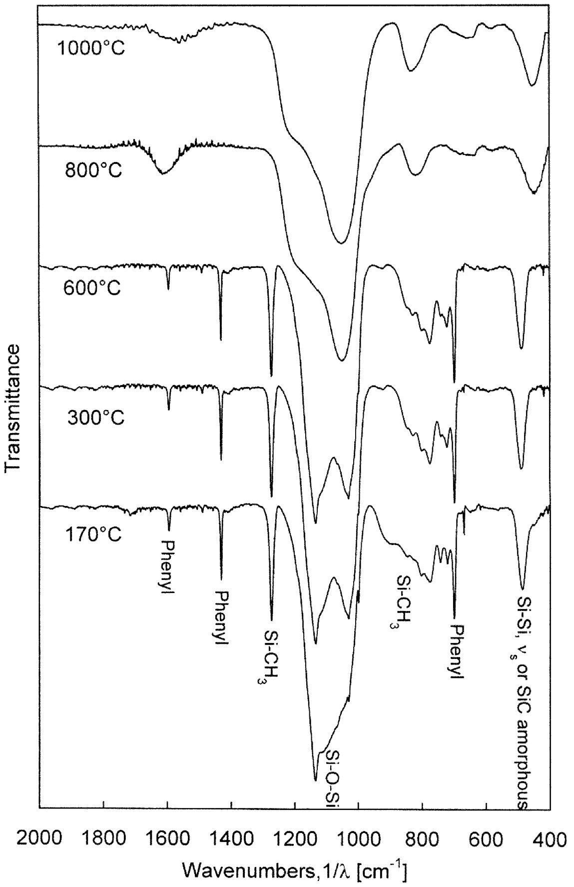


Fig. 5. FTIR investigations from the decomposition of a poly(phenylmethyl) silsesquioxane.

H_2, and probably SiO removal. The pre-existing Si–C bond of the polymeric main chain stayed intact forming the mainly covalent amorphous structure after pyrolysis.[18]

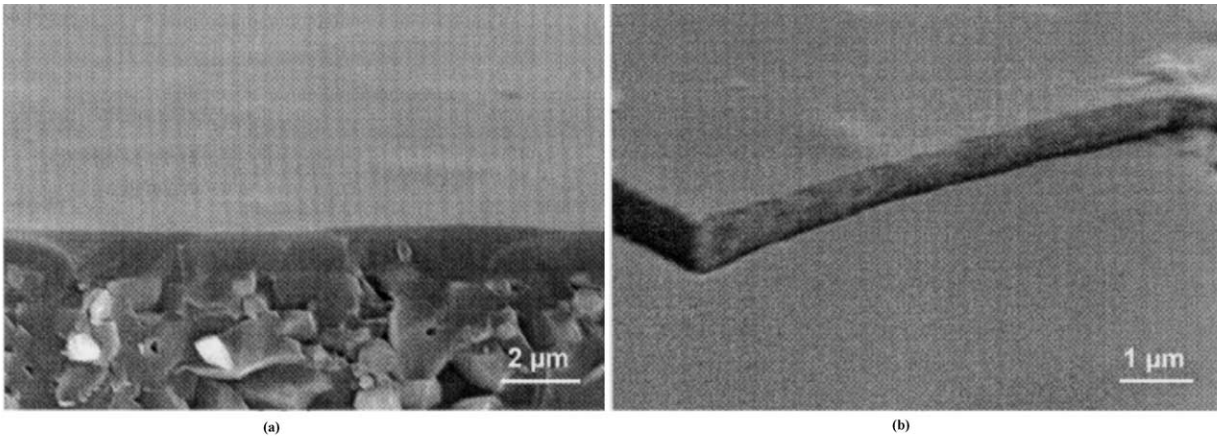
Fig. 5 shows a series of FTIR spectra taken after temperature treatment between room temperature up to 1000 °C under nitrogen. It can be seen that the typical oscillation modes of the precursor side groups (CH_3, SiH) disappear for temperature higher than 600 °C. The pyrolysis is finished at about 800 °C. Basically no significant difference to bulk materials was observed.

3.3. Microstructural investigations

Fig. 6a and b shows micrographs of two coated specimen. These are fractured surfaces after the deposit and ceramisation of the coating. The alumina substrate material (Fig. 6a), as well as the silicon substrate (Fig. 6b) enables a strong adhesion of the same type of coating. The coatings show the typical fracture surface of an amorphous material. No delamination or segmentation cracks were observed.

The fact that the pyrolysis of the spray coating does not lead to any kind of fracture was somewhat unexpected. As can be seen from Fig. 4 the weight loss is in the order of 20–25 wt.%. Thus, a linear shrinkage in the order of several % is to be expected. In a fully strain hindered situation this would create stresses higher than the strength of the material, i.e. crack formation was to be expected. In this case a highly anisotropic shrinkage must be assumed. Most likely the shrinkage parallel to the surface is much smaller than in the orthogonal direction. This effect is known from sol-gel thin film manufacturing. Obviously the surface effect is quite strong and the coating has to been seen as a surface controlled film rather than an independent elastic continuum. Thus a critical thickness exists. For larger thickness a cracking occurs. For siloxane materials this critical thickness is in the order of 3 μm and for carbosilazane 3.5 μm, respectively.

Obviously the solvent content was still high enough to achieve a continuous coating as well as smoothing of the surface roughness, which can be attributed to the surface tension of the precursor solution. Roughness measurements (Table 1, Fig. 7) showed that R_a value of 0.2 μm could be reached. These micro structural obser-



(a) (b)

Fig. 6. Si–O–C coating on an alumina (a) and silicon (b) substrate after pyrolysis at 1000 °C under N_2.

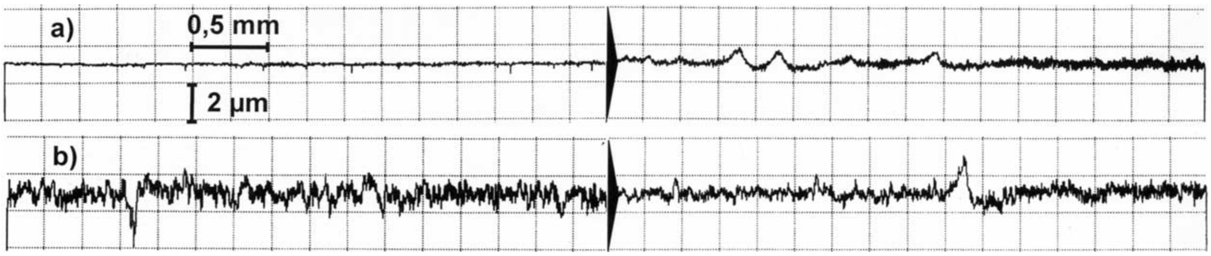


Fig. 7. Surface roughness of an uncoated (left) and coated (right) alumina substrate (a: polished, b: as fired).

vations could be reproduced on alumina (with and without an intergranular glassy phase) silicon wafer, graphite and C/C composites.

The ceramisation process in a furnace requires substrate materials, which can bear the temperature of up to 1000 °C without damage or changes in their microstructure. However, from technical point of view a ceramic coating is most interesting for either materials which behave soft (to produce a hard coating, tribo coating, oxidation protection, etc.) or which are not sufficiently high temperature stable. This problem could be solved by using an ellipsoidal mirror furnace driven by 1000 W halogen lamp attached to a controller. In the focus of this furnace temperatures of up to 1500 °C can be reached. Only the coating is exposed to this heat.

Si–O–C is basically stable up to 1200 °C which implies the use as an oxdiation protection on other materials. Typical cases would be C-fibre reinforced composites.[19–21] The material combination is promising, because C-fibre based materials usually have a very low thermal expansion which meets that of the coating (2.5 10^{-6}/K). Fig. 8 shows a SEM image of a Si–O–C coated C/SiC fibre reinforced material. The productivity of spray coatings (kg/h) is about two orders of magnitude higher than that of CVD-coating.

The microstructure was investigated by cross-sectional transmission-electron microscopy (TEM). Fig. 9 is giving a typical bright-field TEM micrograph of the heterostructure displaying a very smooth surface and an abrupt interface between the Si–O–C layer and the Si (111) substrate. The dark line contrast along the hetero-interface corresponds to a surface region of the Si wafer with a width of only a few monolayers as clearly seen in the high-resolution TEM image in Fig. 10. Its origin is still under discussion. The HRTEM image nevertheless

Table 1
Surface roughness of different uncoated and coated substrate materials

Substrate materials	R_a (substrate)	R_a (coating)
Alumina	0.34	0.24
Alumina—polished	0.03	0.12
Graphite—polished	0.22	0.29
Quartz	0.49	0.18
Steel (St37)	1.24	1.00

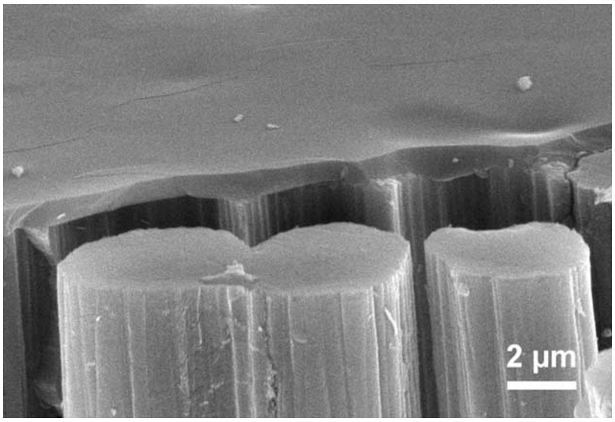


Fig. 8. Fracture surface of a spray coated and pyrolised C-fibre material.

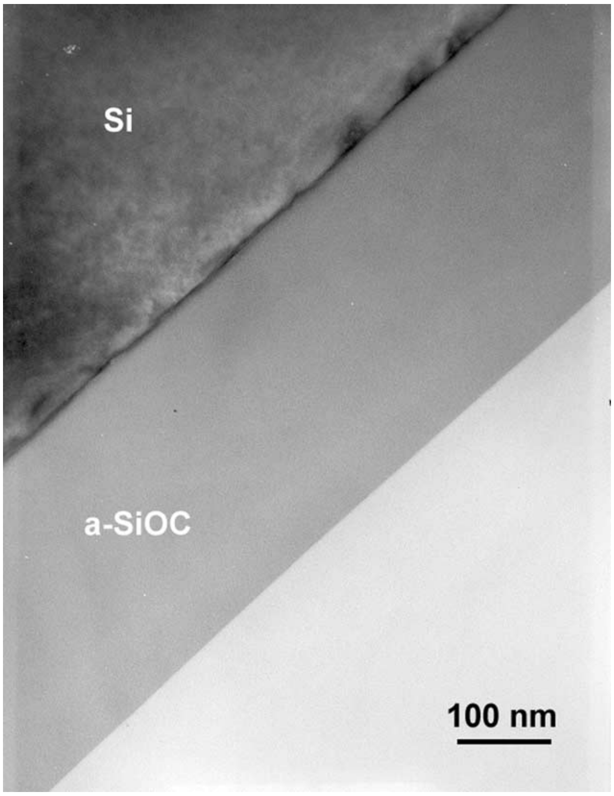


Fig. 9. TEM micrograph of a cross section.

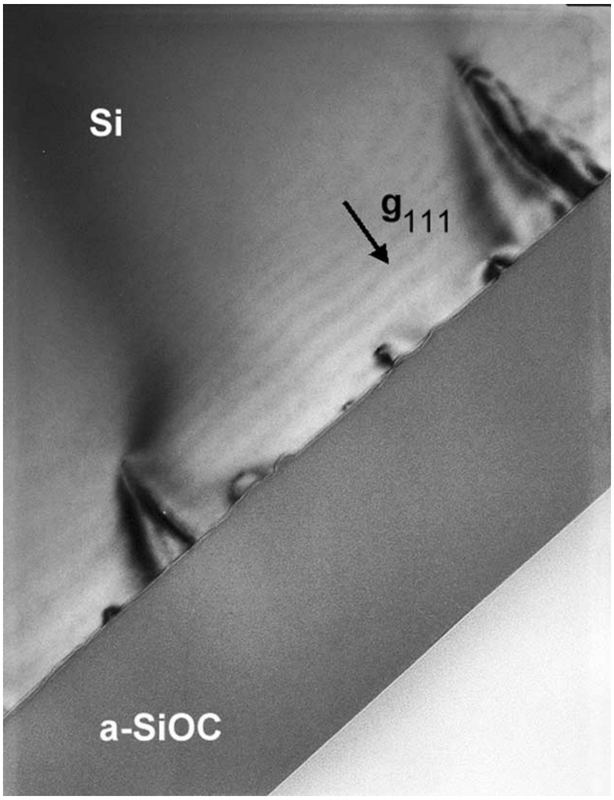


Fig. 10. HRTEM image of the crystalline Si-substrate and the amorphous Si–O–C layer.

reveals along the wide terraces a structurally perfect transition from the crystalline Si to the amorphous Si–O–C layer comparable to the well-known Si–SiO_2 case. The composition of the amorphous film appears uniformly with no evidence for phase modifications, although, on the nanometer scale, small patches are detected indicating the onset of crystallisation because periodic arrangements of atoms and lattice planes can be discerned.

In spite of the strong shrinkage of the films during heat treatment, no strain features or crack-like pattern are observed in the Si–O–C layer. However, strain contrast as well as dislocation lines become visible in the substrate material near the interface if taking a TEM micrograph under g111 (diffraction vector) two-beam conditions (Fig. 10). These defects are the result of plastic relaxation engaging a good absorption between coating and substrate.

4. Summary

- The polymer spraying process has been developed to generate ceramic coatings on different materials by spraying a precursor solution and subsequent pyrolysis.
- The use of polymer solutions was more successful as compared to polymer melting because of too fast polymerisation.
- The two-flux nozzle was found to operation best at 2 bar gas pressure and operation distance of 200–300 mm. The particle size distribution was bimodal composed out of μm-size primary particles and large agglomerates.
- The decomposition of the polymers occurs in a characteristic two-step process, which is basically very similar to bulk materials.
- The interface between coating and substrate is bonding on atomic level without delamination or segmentation cracks.
- The shrinkage on polymerisation and ceramisation was compensated most probably by an anisotropic shrinkage. A critical film thickness of 3 μm was recognised.
- Mirror furnace heating was sufficient to achieve a single side heating to pyrolyse the coating without heating the substrate.

5. Outlook

The open question of the next future is the understanding of the adhesion process from wetting to the final ceramic coating, accompanied by study of the substrates of technical relevance and their surface characteristics. Hence, the process has to test on larger surface areas. Varying the surface chemistry as well as the use of reactive and non-reactive fillers will approach the question increasing thickness.[22–26] Further, the process has to be tested for more critical precursors such as carbosilanes (results in Si–C), carbosilazanes (Si–C–N) and finally borocarbosilazanes (Si–B–C–N).

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