

In situ generated homogeneous and functionally graded ceramic materials derived from polysilazane

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Abstract

The pyrolysis of cross-linked poly(hydridomethyl)silazane pellets via transient isothermal ammonia gas treatment yields amorphous layered ceramic bulk Si/N-Si/N/C-materials with graded carbon content. By this process the C content in the material can be adjusted with high accuracy in the range between 0 and 14 wt.%. The influence of (1) temperature of reactive ammonia treatment (2) time of reactive isothermal ammonia treatment (3) isothermal holding time under inert atmosphere (Ar) before application of ammonia (4) degree of cross-linking of the polycarbosilazane (5) porosity of green compact (6) volume ratio of NH₃ in the reactive atmosphere was examined. The temperature of 525 °C and the reactive atmosphere containing 10 vol.% NH₃ were found to be optimum for carbon content adjustment. Higher ammonia contents did not allow suitable control of the process, while higher temperature of transient heat treatment caused crack formation in the specimen due to excessive pressure of gaseous reaction products. High degree of cross-linking as well as the annealing of cross-linked green bodies at transient temperature in inert atmosphere decrease the efficiency of the reactive treatment and increase the amount of C in the pre-ceramic continuous random network (CRN). Next to graded materials, samples with bulk homogeneous carbon distribution were generated. However, these require more sophisticated heating schedules and combination of reactive treatment with pre-annealing in inert gas.

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1. Introduction

In the last decades a great deal of interest has been focused on non-oxide ceramics, especially on SiC and Si₃N₄. This is mainly because of their excellent mechanical properties at high-temperature, high fracture toughness and outstanding corrosion-resistance. Due to covalent bonds restricting the ability of self-diffusion, these materials traditionally are densified using oxide sintering aids to form crystalline ceramic

parts via liquid phase sintering. To avoid the deteriorating influence of resulting oxide grain boundary phases at room temperature on, for example, fracture toughness,¹ and at elevated temperatures, in particular on internal oxidation,^{2,3} and creep,^{4,5} novel techniques to obtain oxygen-free ceramic materials have been developed. One of these is the so-called “hybrid” technology, based on pyrolytic conversion of metal-organic polymers into amorphous and crystalline ceramics.^{6–9} Pyrolysis is usually conducted under inert atmosphere to avoid oxygen contamination. The initially resulting inorganic continuous random network (CRN) structure was found to be, depending on precursor chemistry and stoichiometry, stable up to 2000 °C.¹⁰ Polysilazane-derived polycrystalline Si₃N₄/SiC/C micro/nano composites proved to be oxidation resistant in air up to 1600 °C.¹¹ The in situ reinforcement

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of Si_3N_4 by SiC-nanoparticles is also facilitated, as was demonstrated for polycarbosilazane-derived polycrystalline composites.¹²

In addition, polymer pyrolysis offers the possibility to apply continuous as well as discontinuous, i.e. transient, reactive gas treatment in order to tailor the stoichiometry of the final product. Commonly, stoichiometries through all processing steps from precursors to inorganic CRNs are distinctly different from the stoichiometry of the desired ceramics, especially with respect to carbon content. Thus reactive heat treatment could prove to be a suitable tool for application-ready tuning of polymer derived materials. The two major properties influenced by carbon are structural stability at elevated temperatures and electrical conductivity. Surplus carbon (C^{free}) not incorporated into the CRN-structure by Si–C-bonds is precipitated within the structure during pyrolysis thus creating voids and large defects. In a previous study we found the micro-scale mechanical properties of pyrolysed polysilazane-derived materials to be impaired by precipitation of free C within the Si–C–N matrix.¹³ Moreover, due to bond rearrangement and significant volume shrinkage, crystallization of the CRN into $\text{Si}_3\text{N}_4/\text{SiC}/\text{C}$ is usually accompanied by deterioration of mechanical properties. During and after crystallization C^{free} reacts with Si_3N_4 yielding SiC and N_2 . With reference to crystalline Si_3N_4 , this reaction has its thermodynamical onset at approximately 1440 °C.¹⁴ On the other hand, increasing content of carbon and especially of C^{free} positively influences the electrical conductivity of the material.

In case of polycarbosilane as well as polycarbosilazane polymers, application of ammonia instead of inert atmosphere during pyrolysis allows for removal of carbon and subsequent formation of pure Si_3N_4 , as it has been shown for continuous NH_3 treatment.^{15–17} A nucleophilic attack by NH_3 and cleavage of Si–C-bonds (at Si– CH_3 -sites) in polysilazane polymers accompanied by evolution of CH_4 has been proposed as the controlling reaction above 400 °C.¹⁸ Both the loss of carbon and the structural changes in the CRN (including crystallization), induce significant changes in electrical properties.^{19,20} In previous papers we reported on the in-situ carbon content adjustment in polycarbosilazane-derived amorphous SiCN bulk ceramics²¹ by transient isothermal treatment, as well as on a simplified mechanistic approach that allows estimation of the range of compositional changes during the reactive heat treatment. This is used to explain the generation of particular Si/N/C compositions from different Si/N/C-yielding precursors.²² In this contribution we focus on separate evaluation of the major processing factors involved, leading to formation of distinct carbon contents and its gradient across the specimen diameter.

The influence of the following parameters on carbon reduction have been evaluated:

- temperature of the isothermal ammonia treatment (i.e. at 500, 525 or 550 °C);
- time of ammonia treatment (specimens were exposed to reactive atmosphere at 525 °C for 0, 5, 7, 9, and 12 h);
- time of isothermal annealing at 525 °C under Ar, preceding the ammonia reactive treatment (dwelling times in pure Ar for 0, 5, 15 and 25 hs);
- degree of crosslinking of the polymer powder, (powder cross-linked at 400 or 600 °C);
- the total open pore volume and the mean pore size of the green powder compacts;
- the concentration of NH_3 in the reactive atmosphere (10, 22, 50, 100 vol.%).

Finally a set of samples with homogeneous carbon distribution all over the sample volume was prepared.

2. Experimental

All experiments were conducted with the preceramic Si/N/C(H)-precursor poly-(hydridomethyl)-silazane NCP200 (not commercially available any more) (Nichi-men Corp., Tokyo, Japan). The polymer was cross-linked under flowing Ar in a quartz tube at 400 or 600 °C. The cross-linked infusible polymer was then ball-milled and sieved through a 32- μm mesh screen. Surface area of the powders was determined by CO_2 -BET (Quantachrom Autosorb-3B). The powder was isostatically pressed for 2 min at 200 or 500 MPa in a silicon rubber die to yield cylindrical green bodies with diameter of approximately 28 or 26 mm, respectively. The mean diameter of open pores in the pressed green bodies was determined by mercury intrusion porosimetry (Micromeritics Poresizer 9320). Pyrolysis was carried out in a quartz tube under flowing Ar in a horizontal SiC electrical tube furnace. The heating rate was 0.5 K/min up to 1100 °C, the exceptions are noted. Transient isothermal reactive ammonia treatment was carried out as an intermediate step at 500, 525 or 550 °C. Mixtures of Ar with 10, 22, or 50 vol.% NH_3 or pure NH_3 were applied as reactive atmospheres. A flow rate 6 l/h and the various gas mixture compositions were adjusted using a Brooks 5850 flow rate controller with gas specific ports. High purity Ar and ammonia (both 99.999, Linde AG, Germany) were used, carefully dried in front of the flow meter inlet. For detailed information on all processing refer to Ref. 21.

The thickness of the layers and/or graded areas was measured on ground cross sections of the pyrolysed specimens. Thereafter the layers were mechanically separated for the carbon content measurements. Carbon content of the respective layers was determined by a hot gas extraction method using a carbon determinator, type EC-12 (LECO-Corp., USA). The measured values

for carbon content determination have a standard deviation within $\pm 1.5\%$ of the measured value. For layer thickness a standard deviation of less than $\pm 5\%$ of the measured value was derived. The thickness of the graded area was estimated by optical microscopy or fractional hot gas extraction.

Investigation of electrical properties was carried out by measuring the complex impedance of the materials in the frequency range between 20 Hz and 1 MHz using a fully automated autobalance bridge (HP 4284 A, Hewlett Packard, USA). Taking into account the geometry of the samples, electrical d.c.-conductivity was calculated. For further details refer to Ref. 23.

3. Results and discussion

The BET measurement revealed significant differences in surface properties of cross-linked, milled and sieved powders. The specific surface of powder A cross-linked at 400 °C was determined to be 270 m² g⁻¹ and no pores were present on particle surfaces. Cross-linking at 600 °C yielded powder B with particles containing nanopores (the mean pore size 2.5 nm) and with much higher specific surface (400 m² g⁻¹). Various pressures applied in the process of specimens shaping yielded the green bodies with significantly different pore structures. The mean diameter of pores in the green body pressed from powder A at 200 MPa was 340 nm, as opposed to

the mean pore size of 180 nm in the green body pressed at 500 MPa.

Table 1 summarizes the results of cross-linking and pyrolysis. All specimens were prepared from powder A, with the only exception of sample 9 where the green body pressed from powder B was used for pyrolysis.

Figs. 1–6 visualize separately the results for the variation of each parameter evaluated. Increasing temperature of the isothermal treatment in ammonia resulted in accelerated carbon removal from the pyrolysed body (Fig. 1). At temperature less than 500 °C carbon reduction did not occur in reasonable time. Increased temperature of transient reactive gas treatment accelerated the velocity of reactions contributing to carbon removal. The main problem to be faced at higher temperature is the rising pressure of the gaseous by-products of the reactions due to insufficient out-gassing through the pore channels. This, at temperature equal or higher than 550 °C, lead to severe cracking of the treated pellets. The isothermal reaction treatment was therefore conducted at 525 °C in the following experiments.

Fig. 2 relates the carbon content of a reference sample (13.5 wt.% C content) pyrolysed without the transient reactive step with the specimens annealed in reactive atmosphere containing 10 vol.% NH₃ at 525 °C.

From Fig. 2 it can be seen that ammonia treatment at intermediate stages basically results in formation of a core/shell structure with respect to carbon content. As

Table 1
Sample denotation and processing data [$T(^{\circ}\text{C})/t(\text{h})$ indicate temperature and time of respective isothermal heating step]

Sample	CIP pressure (MPa)	Pre-treatment in Ar $T(^{\circ}\text{C})/t(\text{h})$	Reactive treatment in NH ₃ $T(^{\circ}\text{C})/t(\text{h})$	NH ₃ ratio (vol.%)	C (wt.%) surface layer	C (wt.%) core
1	200	525/5	–	–	13.5	13.5 ^a
2	200	–	525/5	10	6.3	6.7
3	200	–	525/7	10	1.3	5.7
4	200	–	525/9	10	0.7	1.1
5	200	–	525/12	10	0.3	0.3
6	500	–	525/8	10	1.0	5.8
7	500	525/5	525/8	10	1.5	6.3
8	500	525/15	525/8	10	4.2	7.2
9	500	525/5	525/8	10	3.2	7.6
10	500	500/5	500/8	10	12.2	13.1
11	500	550/5	550/8	10	1.2	1.8
12	200	525/5	525/8	10	1.4	5.2
13	500	525/5 + 8	–	10	16.1	16.1
14	200	0 ^b	–	–	14.4	14.4 ^a
15	500	525/5	525/5	10	9.7	9.9 ^c
16	500	525/25	525/12	10	5.9	5.9
17	500	525/5	550/8	22	2.1	2.1 ^c
18	500	525/5	525/20	10	1.9	1.9 ^c
19	200	525/5	525/20	100	0.5	0.5
20	500	525/5	525/8	50	1.3	4.8
21	500	525/5	525/8	100	1.2	4.5

^a Pyrolysis up to 1000 °C.

^b Continuous heating with 2.5 °C/min after crosslinking.

^c Heating rate 25 °C/h.

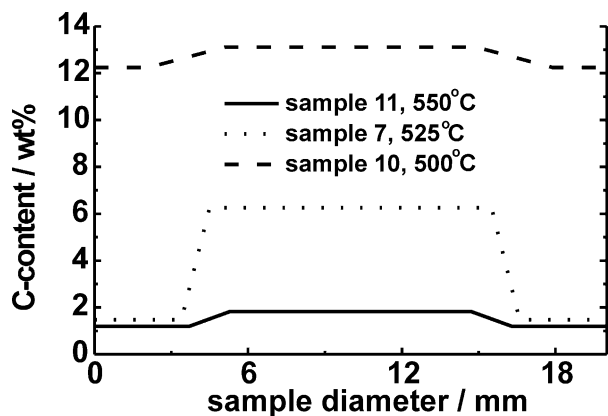


Fig. 1. The carbon content profiles in the specimens heat-treated for 8 h in reactive atmosphere containing 10 vol.% NH_3 in Ar, at 500, 525 and 550 °C.

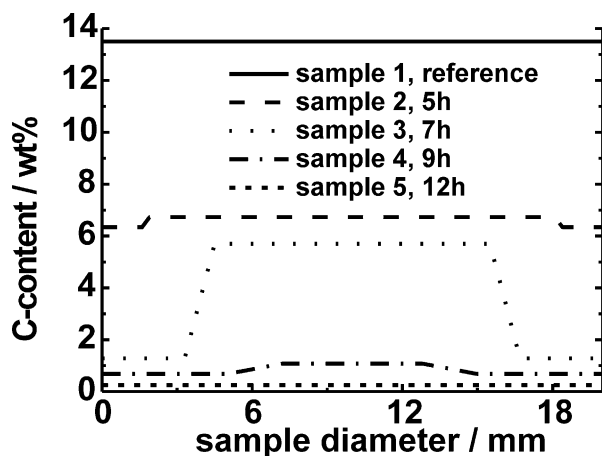


Fig. 2. Topochemical analysis of a reference sample (sample 1) and samples heat-treated 5, 7, 9 and 12 h in the reactive atmosphere (Ar + 10 vol.% NH_3) at 525 °C.

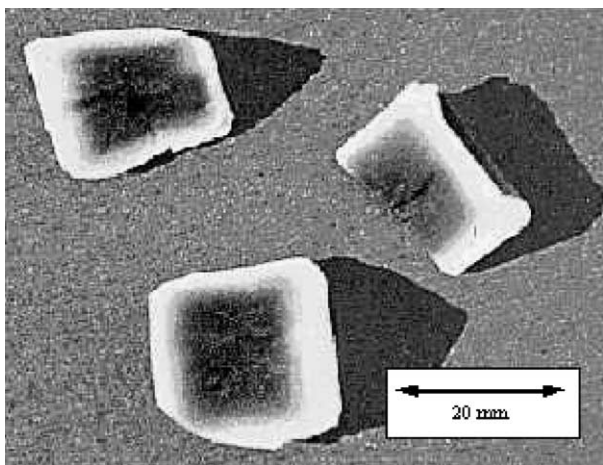


Fig. 3. Surface layer/core structure of the pyrolysed specimen transiently heat-treated 8 h at 525 °C in the reactive atmosphere (Ar + 10 vol.% NH_3).

an example, the core/shell structure of a specimen reactively heat treated for 8 h at 525 °C in (Ar + 10 vol.% NH_3) atmosphere is shown in Fig. 3. An accelerating movement of the core/shell border towards the pellet center was observed with prolonged dwelling times at the transient temperature, see also Fig. 4a. This phenomenon becomes clear by considering the fact that decrease in carbon content in the course of reaction is accompanied by decreasing counterpressure of H_2/CH_4 within the body. This increasingly facilitates access of NH_3 to reaction sites. However, the decrease in carbon content itself is approximately linear with time (Fig. 4b).

Fig. 5 shows the time dependence of carbon content in specimens pre-treated under inert atmosphere (Ar) before reactive annealing in ammonia was applied. Such pre-treatment led to pronounced incorporation of carbon into the pre-ceramic CRN by formation of Si–C bonds by dehydrocoupling and other gas evolving reactions.²⁴ The inertness of C towards ammonia is a result of two factors: strong chemical covalent bonding of carbon atoms with adjacent Si and N atoms in the CRN and steric hindrance, i.e. the reaction cannot occur because there is no direct access of the NH_3 molecules to carbon atoms built into the pre-ceramic network. By this, the effectiveness of the reactive treatment decreases and the average carbon content after ammonia treatment is shifted to higher values. The samples No. 5 and 16 (Table 1) may serve as an additional example. Sample 5 was not pre-treated in Ar and the concentration of carbon was homogeneously reduced down to 0.3 wt.% all over the specimen bulk after 12 h of ammonia treatment at 525 °C. As opposed, in specimen 16, pre-treated 25 h at 525 °C in Ar, a carbon concentration of 5.9 wt.% was achieved after 12 h in NH_3 at 525 °C. Again, the concentration of C was constant all over the specimen volume. It is worth noting (see also Fig. 5) that the Ar pre-treatment reduces the resulting differences in carbon content between the core and a surface layer, and homogeneous distributions of C all over the specimen volume can be readily achieved. It is suggested that the fraction of carbon built in the CRN during the Ar pre-treatment is distributed homogeneously all over the specimen volume. This fraction does not react with NH_3 , thus effectively reducing the counterpressure of gaseous reaction products that normally hinders access of ammonia to the pellet center. This in turn accelerates the movement of the reaction front towards the center leaving behind the constant level of network-forming carbon achieved in the course of the Ar pre-treatment.

Fig. 6 denotes the influence of the state of cross-linking achieved by variation of the cross-linking temperature ($T_{\text{crossl.}} = 400$ °C/600 °C) on the resulting carbon content. Though surface area of the powder B as well as the porosity of the green body compacted from powder B by cold isostatic pressing (sample 9) are both significantly higher than those of sample 7 prepared from

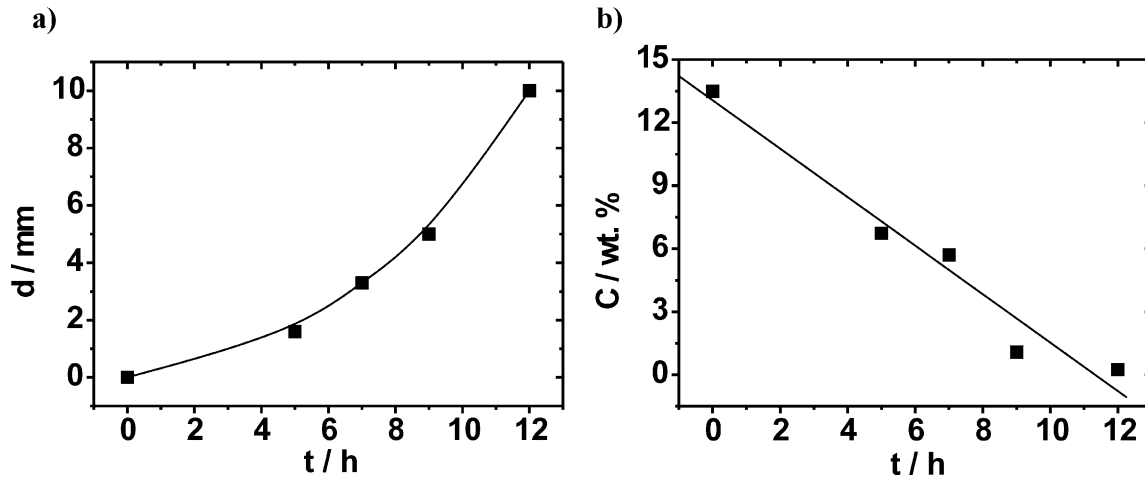


Fig. 4. Time dependence of the carbon content in the core of a specimen pyrolysed at 525 °C (a) and the time dependence of the thickness of carbon-depleted surface layer (b).

less cross-linked powder A, sample 9 retains a higher carbon content after ammonia treatment. Similarly to the effect mentioned above (Fig. 5), the higher temperature of cross-linking resulted in incorporation of a significant fraction of C into the three-dimensional

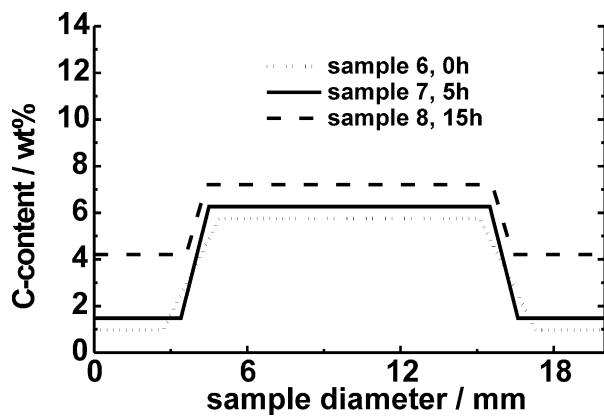


Fig. 5. The topochemical analysis of pyrolysed samples pre-treated for 0, 5, and 15 h under Ar at 525 °C before the reactive atmosphere (Ar + 10 vol.% NH₃) was applied.

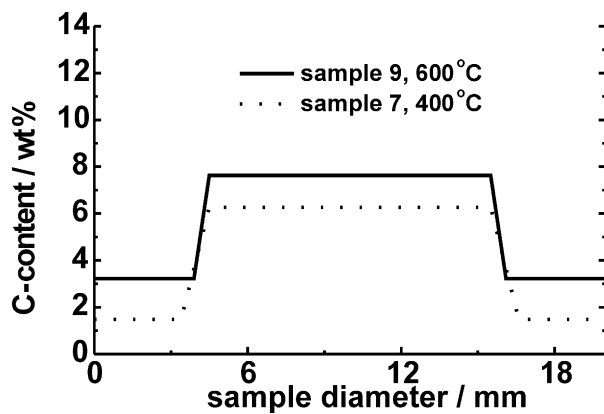


Fig. 6. Influence of the cross-linking temperature on carbon profiles in pyrolysed pellets. ($T_{\text{crossl.}} = 400 \text{ °C} / 600 \text{ °C}$).

pre-ceramic network, leaving less $-\text{CH}_3$ (methyl) groups to be eliminated by ammonia. It is worth noting that the pellets prepared by pyrolysis of the green bodies from overcross-linked powders lack mechanical stability. This is a consequence of the lower amount of methyl groups available in highly cross-linked powder as potential bridging C-providers for formation of chemical bonds between adjacent powder particles and for constructing the CRN during pyrolysis.

Fig. 7 shows the influence of accessible open porosity in the green body on the residual carbon content after pyrolysis. The difference in the mean pore diameters accounts for differences in residual carbon content and a slight deviation in gradient. There are several parameters that account for observed difference. The smaller mean diameter of open pores and lower overall porosity provide a smaller effective reaction area accessible to ammonia. At the same time narrower pore channels hinder the inward diffusion of ammonia into the body, as well as outward diffusion of gaseous reaction products

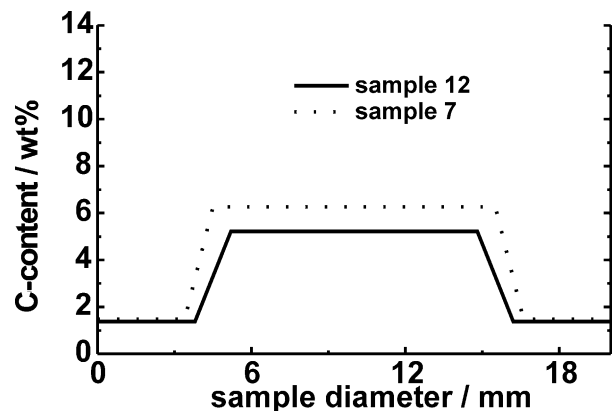


Fig. 7. Influence of the mean pore size of the green body on carbon content in pyrolysed specimens heat-treated 8 h at 525 °C in Ar/NH₃ (10 vol.% NH₃) atmosphere. The mean pore size is 340 and 180 nm for samples 12 and 7, respectively.

(CH₄ and other hydrocarbons). Increasing pressure of hydrocarbons inside the pore channels both further hinders access of ammonia to reaction sites and shifts the reaction equilibria towards the reagents. The total contact area of powder particles increases with the applied compacting pressure thus allowing better mutual bonding of adjoining grains by the formation of large number of bridging C–C-bonds among the individual particles of the cross-linked polymer. Improved mechanical strength of such specimens can be then expected.

Reaction speed was also influenced to certain extent by the relative amount of ammonia in the reactive gas mixture. Fig. 8 indicates that the dependence of the residual carbon content on the volume ratio of NH₃ is non-linear. The residual carbon content is practically indifferent to the NH₃ volume ratio at the NH₃ concentrations higher than 50 vol.% and approaches the value of approximately 1.2 wt.%. This value can be, with reasonable certainty, considered as the fraction of C built into the CRN during the cross-linking step and in the course of 5 h pre-annealing of the specimens in the inert atmosphere.

The previous paragraphs illustrate possibilities for preparation of graded material that typically require only a relatively simple heat treatment schedule. Similarly, samples with high carbon content (approx. 14 wt.%) homogeneously distributed all over the sample volume, or those completely depleted of carbon require only plain continuous annealing in inert, or reactive atmosphere, respectively. On the other hand, more sophisticated heating schedules that generally include a pre-annealing step in inert atmosphere followed by transient isothermal reactive heating in ammonia and pyrolysis are required for preparation of amorphous Si–C–N-based materials with intermediate concentrations of carbon homogeneously distributed all over the volume. As stated before, the incorporation of C into the ceramic CRN as bridging Si–C bonds play a key role. This carbon appears to be inert with respect to

ammonia. The slight deviation in core/shell-content of carbon (e.g. sample 15, Table 1) is a result of competition between outgassing of CH₄ and incorporation of C into CRN in the course of pre-annealing in inert gas and subsequent ammonia treatment. In accordance with the results presented earlier, we suggest that either inert annealing already introduced that small carbon gradient due to facilitated outgassing of CH₄ from the surface layer, or that for a certain time span after the pre-annealing the counterpressure of evolved CH₄ still impeded ammonia access to sub-surface sites, or a combination of both.

As demonstrated, the carbon content can be adjusted by suitable treatment schedules over a range from 0.2 wt.% to more than 14 wt.%. This results in a variation of electrical properties. Fig. 9 exemplarily illustrates the differences in dc-conductivity of two amorphous Si/C/N ceramics as calculated from impedance spectroscopy results, and its variation with temperature. Sample 19 with approximately 0.5 wt.% C-content is compared to sample 1 with 13.5 wt.% of C. Adjusting the C-content from 13.5 to 0.5 wt.% by ammonia treatment decreases the dc-conductivity over the whole measured temperature range by approximately four orders of magnitude.

Relatively simple preparation of specimens with different concentrations of carbon in a surface layer and in the core, as mentioned earlier, opens the possibility for easy preparation of the materials functionally graded with respect to their electrical properties. Fig. 10 highlights the range of dc-conductivity that can be covered by polysilazane-derived samples through reactive ammonia treatment, non-reactively pyrolysed samples, and also with subsequent ageing at elevated temperatures (between 1100 and 1450 °C). This is put into context with dc-conductivity values of a range of insulating and conducting materials. It can be seen that by appropriate treatment of the Si/C/N ceramics, nearly the whole conductivity range of insulators and semiconductors is

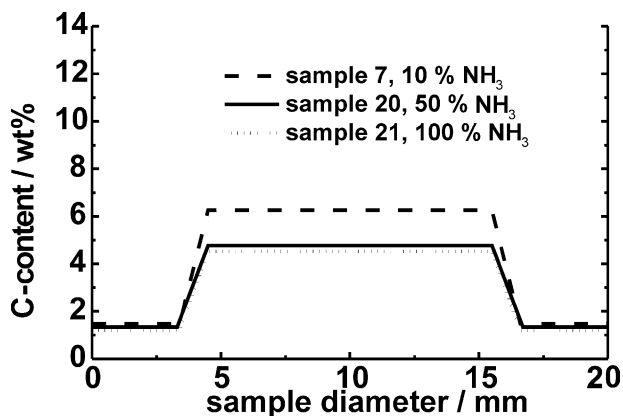


Fig. 8. Influence of volume fraction of NH₃ in the reactive Ar/NH₃ atmosphere (10, 50 and 100 vol.%) on the carbon content in pyrolysed specimens heat-treated 8 h at 525 °C.

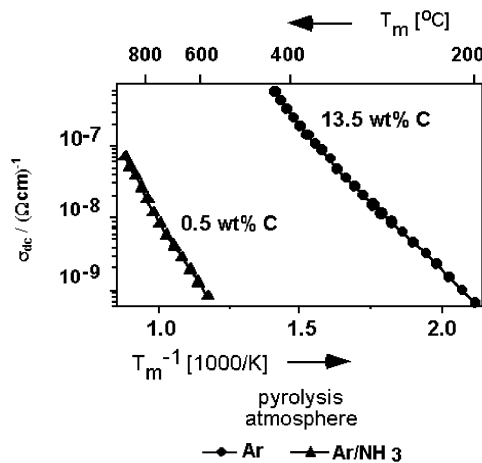


Fig. 9. Variation of dc-conductivity of amorphous Si/C/N ceramic body with measuring temperature and C-content.

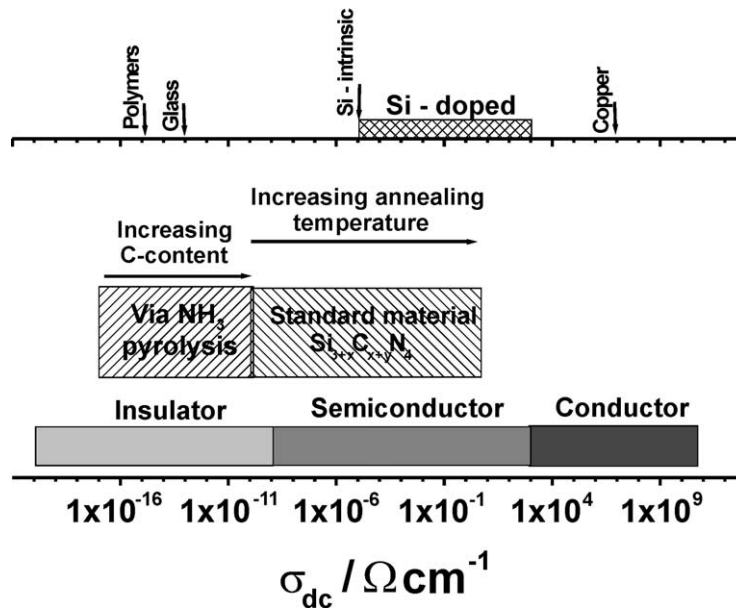


Fig. 10. dc-Conductivity σ_{dc} (Ωcm^{-1}) of various materials at 20 °C.

readily adjustable. The insulating properties increase with decreasing C-content, reaching for carbon concentrations approaching zero values close to those characteristic for the Si_3N_4 . As opposed, the standard material with approximately 13–14 wt.% carbon exhibits a room temperature conductivity in the range typical for semiconductors. The room temperature conductivity increased with increased annealing temperature applied to untreated samples. This is due to thermally activated relaxation and rearrangement processes involving the $\text{SiC}_x\text{N}_{4-x}$ -tetrahedrons of the CRN ceramic material as well as precipitation of C^{free} into the voids of the CRN-structure.

4. Conclusions

It was demonstrated that the carbon content as well as the layer thickness of polysilazane-derived non-crystalline ceramics can be tailored by transient ammonia treatment deliberately to a great extent. Processing parameters of major importance are temperature and time of isothermal ammonia application as well as the time of isothermal annealing in inert atmosphere preceding the reactive gas treatment. This offers the chance to design functionally graded materials with respect to electrical and mechanical properties, as well as materials with homogeneous carbon distribution all over the sample. It was shown that electrical properties like dc-conductivity strongly depend on the actual carbon content. This yields for example an opportunity for the preparation of new high temperature resistant electrical conductors, mechanically reinforced by insulating Si_3N_4 -coatings.

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