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Dense Silicon Carbonitride Ceramics by Pyrolysis of Cross-linked and Warm Pressed Polysilazane Powders

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Abstract

This study reports on the pyrolysis and densifaction behavior of cross-linked poly(hydridomethylsilazane) powders. The influence of the cross-linking procedure such as temperature and annealing time of the polymer powders on the compaction behavior under cold and warm pressing conditions is discussed. The degree of cross-linking is determined by thermal mechanical analysis (TMA). In addition to particle sliding which is assumed to be the compaction mechanism obtained by cold-pressing, the polymer powder consolidates by plastic deformation applying warm-pressing. A continuous 3-dimensional polysilazane network is formed after a dwelling time under these conditions. Pyrolysis of the cross-linked and compacted polysilazane powder in argon at 1100°C gives crack-free amorphous silicon carbonitride $Si_{3+x}C_{x+y}N_4$ *with compositions ranging from* $x=1{\cdot}47$ *and* $y=0{\cdot}88$ *for cold pressed samples to* $x=1{\cdot}47$ *and* $y=1{\cdot}86$ *for warm pressed materials. The residual open porosity is significantly reduced from 10–15 vol% in the cold pressed specimens to 1·3–5 vol% by the warm pressing procedure. The weight loss during pyrolysis between room temperature and 1300°C is about 5 wt% lower than that for cold pressed specimens. This result is explained by a reduced methane evolution during the polymer-to-ceramic conversion and is in accordance with the enhanced carbon content of the warm pressed material. © 1999 Elsevier Science Ltd. All rights reserved*

Keywords: silicon carbonitride, precursors-organics, pressing, SiC, Si_3N_4.

1 Introduction

Precursor-derived amorphous silicon carbonitride (SiCN) ceramics are promising materials for high temperature applications. Depending on the stoichiometry, they do not tend to crystallize or degrade up to $T \leq 1350°C$ in inert atmospheres (Ar, N_2). In air, they are stable up to 1500°C.[1–4] These findings make the SiCN ceramics good candidates for application in oxidative environments.[1] Creep hardening after long term deformation at 1000 and 1300°C in N_2 without devitrification was reported recently for polysilazane-derived SiCN bulk ceramics.[5] The creep viscosity of amorphous SiCN at 1300°C was analyzed to be three orders of magnitude higher than that of fused silica.[5]

However, the preparation of dense bulk ceramics encounters difficulties which are in part associated with the outgassing of hydrogen and hydrocarbons during the polymer to ceramic transformation. Cold isostatic pressing of polysilazane powders and subsequent pyrolysis of the green compacts result in amorphous SiCN bulk ceramics with a noticeable open porosity of <10 vol%.[6,7] Recently, it was shown that compaction of polysilazane powders by uniaxial pressing at elevated temperatures denoted as warm pressing can provide SiCN ceramics with a reduced residual open porosity as low as 3 vol%.[8] In the present work, the warm pressing behavior of differently cross-linked polyorganosilazane powders has been investigated. The influence of the open porosity of cold and warm pressed polysilazane green compacts on the residual porosity of the SiCN ceramics after pyrolysis is discussed. The intention of this study was to elaborate the processing conditions under which compacted polysilazane powders can be transformed to dense SiCN bulk ceramics.

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2 Experimental

2.1 Materials preparation

2.1.1 *Cross-linking*

Poly(hydridomethyl)silazane (NCP200, Nichimen Corp., Tokyo, Japan) was thermally cross-linked with a heating rate of 600°C h^{-1} under different conditions in flowing argon (99·999% purity, gas flow 6 dm^3 h^{-1}), milled in a polyethylene jar with zirconia milling balls for 15 h and sieved through a 32 μm screen. The sample notation and cross-linking conditions are listed in Table 1. Cylindrically shaped specimens with 9 mm in diameter and 7 mm in height were prepared by cold isostatic pressing at 500 MPa (samples S1–S3) or cold uniaxial pressing at 630 MPa (sample S4) of sieved and cross-linked polysilazane powders. The degree of cross-linking of the polysilazane powders was evaluated by thermal mechanical analysis (TMA) of the green compacts performed with a Netzsch TMA 402 equipment. Mercury pressure porosimetry (Micromeritics Poresizer 9320) was applied to quantify the open porosity of both green and pyrolysed bodies (Table 1).

2.1.2 *Warm pressing*

The powders were also uniaxially warm-pressed in a steel dye with a heating mantle at temperatures between 70 and 380°C (Paul-Otto Weber GmbH, PW-40, Germany). The specimens were heated to the applied temperature under pressure (470 MPa) with a heating rate of 300°C h^{-1}. The maximum temperature was held for 0.5 h at 470 MPa, followed by 0·5 h at 630 MPa or for 0·5 h at 710 MPa (sample S4). After deloading, the specimens were cooled down to room temperature within 2 h.

2.2 Pyrolysis and characterization

The cold or warm pressed polysilazane compacts were heated with 5°C h^{-1} in flowing Ar up to 1000 or 1100°C and held 4 h at the final pyrolysis temperature. Bulk densities of the green and pyrolysed specimens were determined by the mercury immersion method. The volume fraction of open pores as well as the pore size distribution were measured either by BET (Quantachrom Autosorb-3B) or by mercury pressure porosimetry (Table 1). The weight fraction of carbon in the pyrolysed samples was analyzed using a LECO EC12 carbon determinator. The nitrogen content and the oxygen contamination were determined simultaneously with a LECO TC436 N/O determinator. The analysis of prepared SiCN ceramics revealed 16·5 wt% C and 23·3 wt% N in the warm pressed samples compared to 13 wt% C and 25 wt% N in the specimens compacted by cold isostatic pressing. The silicon content was calculated as the difference of the sum of the C, O and N content to 100%. The oxygen contamination was 1·8 wt% for the cold pressed sample S2 and 5·5 wt% for the warm pressed sample S1. No significant deviation of the analytical data were found for the samples S1–S4.

Thermal gravimetric analysis (TGA) coupled with mass spectroscopy (MS) were performed with sample S3 to study the pyrolysis behavior of cold and warm pressed specimens. The experiments were run with a Netzsch STA 429 simultaneous thermal analyzer and Balzers QMG421 quadrupol mass spectrometer in flowing Ar between room temperature and 1300°C with a heating rate of 5°C min^{-1}.

3 Results and Discussions

3.1 Cross-linking

Poly(hydridomethyl)silazane can be thermally cross-linked between 200 and 450°C in inert atmospheres. This procedure gradually increases the softening point of the polymer and finally transforms it to an infusible material. The main reactions involved during cross-linking have been recently summarized by Seyferth *et al.*[9] At temperatures between 500 and 1000°C, the polymer

Table 1. Specimen notation and conditions applied for cross-linking and cold or warm pressing of poly(hydridomethyl)silazane powder; heating rate: 600°C h^{-1} up to the cross-linking temperature. The open porosities before and after pyrolysis are listed as determined by BET or mercury pressure porosimetry

			Cold-pressing:	*Warm pressing*		*Pyrolysis*[b]
Specimen	*Cross-linking temperature [°C]*	*Annealing time in Ar*[a] *[h]*	*Porosity [vol%] before/after pyrolysis*[b]	*Temperature [°C]*	*Porosity [vol%]*	*Porosity [vol%]*
S1	400	2	7·7/ > 30	320	$\leqslant$0·5	1–3
				$\geq$360	11·2	4·3
S2	400	3	11·5	280–340	0·8–1·6	1–3·3
				$\geqslant$360	17·8	5
S3	420	3	16·5/10·8	300	1	1–2·5
S4	380	1·25	23·0/14·9[c]	340	5·6	1·3[c]

[a] All the samples were subsequently annealed for 1 h in vacuum at 10^{-3} Torr at the cross-linking temperature.

[b] Pyrolysis was conducted under flowing Ar at 1100°C, dwell time 4 h.

[c] Pyrolysis under Ar at 1000°C, dwelling time 4 h.

undergoes extensive decomposition and forms amorphous silicon carbonitride.[10] The polysilazanes cross-linked under different conditions (samples S1–S3) as listed in Table 1 were characterized by thermal mechanical analysis (TMA) and the results are shown in Fig. 1. It is evident that Sample S1 softens above 270°C indicating a relatively low degree of cross-linking. In contrast, samples S2 and S3 cannot be fused. With increasing temperature, the specimen S2 shows two consecutive length changes, while sample S3 continuously shrinks in one step between 440 and 800°C. The total relative linear shrinkage at 1000°C is found to be 21·9% for S2 and 11·7% for S3.

3.2 Polymer powder consolidation

The pore size distributions of cold isostatically pressed cross-linked powders S1-S3 measured by mercury pressure porosimetry are shown in Fig. 2. The open porosity of the compacted polysilazane S1 is 7·7 vol% while that of S2 and S3 is determined to 11·5 and 16·5 vol%, respectively. This finding shows that the higher the degree cross-linking the lower the deformability of the polymer particles. Consequently higher open porosities of the extensively cross-linked polymer powder compact are found. In S1, the pores with diameter smaller than 0·1 μm are nearly completely eliminated whereas a significant amount of pores with diameters above 0·1 μm is detected, in particular for S3.

Warm-pressing of S1–S3 powders at T ($\leq$340°C yields translucent polysilazane green compacts with open porosities $\leq$2 vol% (Table 1). In contrast, the volume fraction of the porosity increases up to 17·8 vol% if temperatures exceeding 360°C are applied during warm-pressing. As determined by BET, mainly nanopores with diameters between 2 and 5 nm are present. The increase in porosity is assumed to be related to the pronounced polycondensation giving off volatile gases (e.g. ammonia or methane) at temperatures exceeding 350°C.[10]

Uniaxial pressing of cross-linked polysilazane powder (initial particle size < 32 μm) at various temperatures (25–340°C) using a dwelling time of 30 min significantly influences the final bulk density of the prepared green bodies. With increasing pressing temperatures a significant increase of the green density of the polysilazane precursor is observed (Fig. 3) The densification of the polymeric material applying pressing temperatures below 200°C is explained by particle arrangement and particle sliding. Figure 4(a) reveals the microstructure of a fracture surface of uniaxially cold pressed polysilazane powder (sample S4). Interconnected polymer particles can be distinguished from packing faults which lead to open porosity in the ceramic matrix developed at higher temperatures. Enhanced densification is obtained by pressing temperatures exceeding 200°C. Due to plastic deformation of the precursor material, open pores and voids between distinct precursor particles of the green sample are eliminated. Warm pressing at temperatures above 260°C is accompanied by another densification mechanism. Here, further intra- and interparticular cross-linking reactions

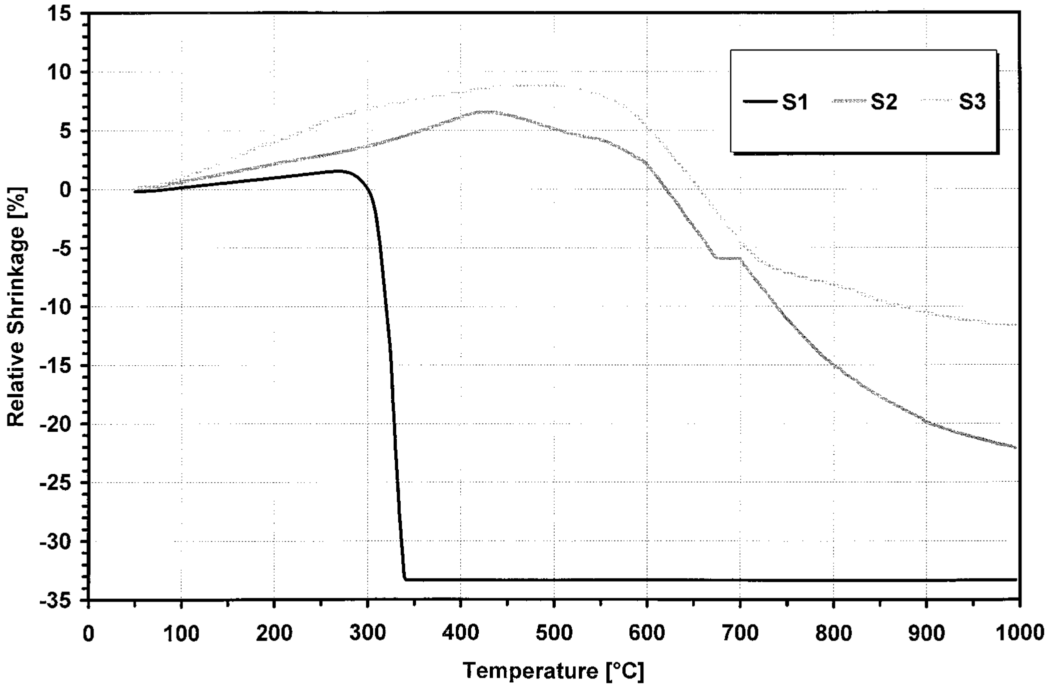

Fig. 1. Thermal mechanical analysis (TMA) of cross-linked and cold isostatically pressed polysilazane powders S1, S2 and S3 between room temperature and 1000°C in flowing Ar, heating rate 300°C h^1.

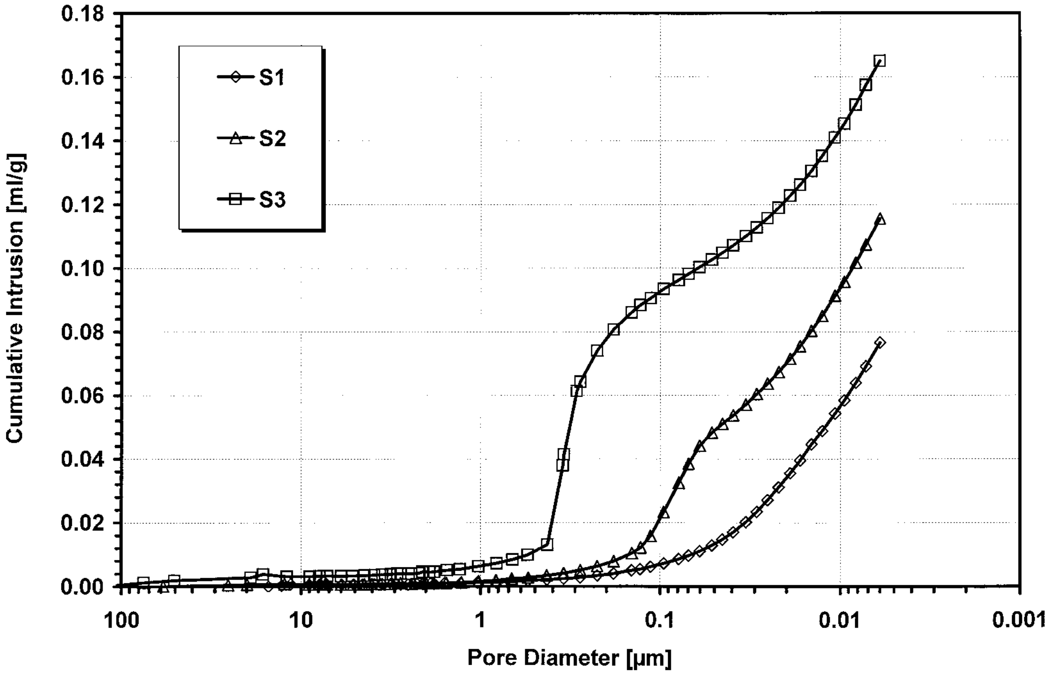

Fig. 2. Cumulative intrusion curves of cross-linked and cold isostatically pressed polysilazane powders S1, S2 and S3 measured by mercury pressure porosimetry.

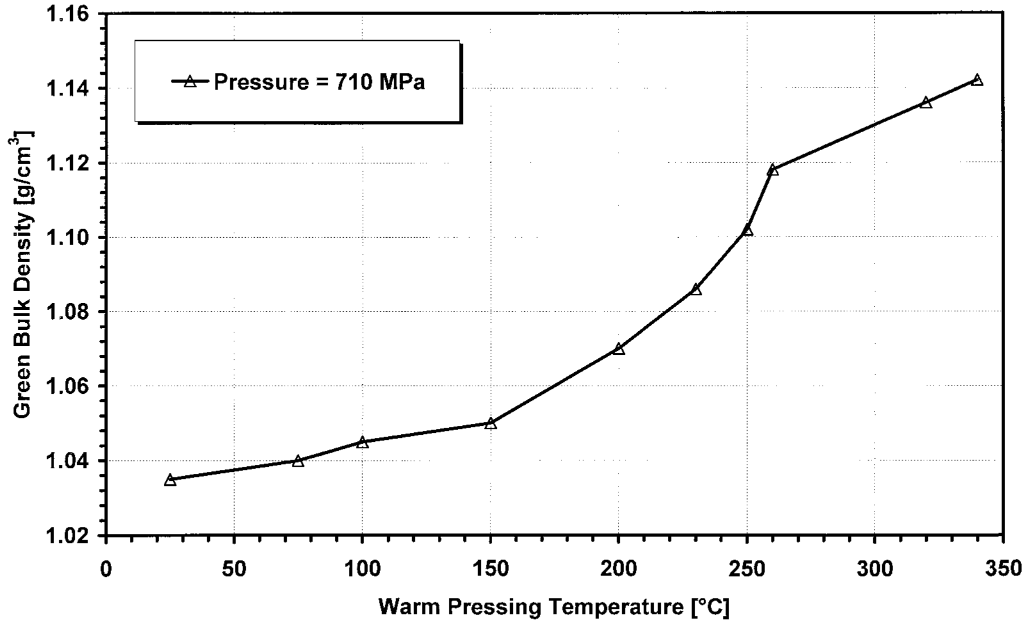

Fig. 3. Temperature - density curve of cross-linked and uniaxially warm pressed poly(hydridomethyl)silazane powder.

take place with the result that the polysilazane particles are successively welded together. Figure 4(b) represents the typical microstructure of a uniaxially warm pressed polysilazane specimen (sample S4). As a conclusion of these findings the following schematic depicted in Fig. 5 summarizes the densification of cross-linked polysilazane powders by uniaxial cold and warm pressing.

3.3 Pyrolysis

Pyrolysis of the cold-isostatically pressed specimens at 1100°C in Ar resulted in the formation of bulk amorphous SiCN ceramics with open porosities of 10·5 and 10·8 vol% for samples S2 and S3, respectively. Due to the low degree of cross-linking, sample S1 bloated during pyrolysis by transient softening of the polysilazane with simultaneous outgassing of H_2 and CH_4 as determined by mass spectroscopy reported by Ziedel and Dreßler.[11] An open porosity exceeding 30 vol% is developed under these conditions. In contrast thermal decomposition of warm pressed samples S1–S3 yields dense SiCN bodies with open porosities between 1 and 5 vol% (Table 1). The pyrolysis of sample S2 warm pressed at 200°C yields a severely bloated ceramic body. This behavior is attributed

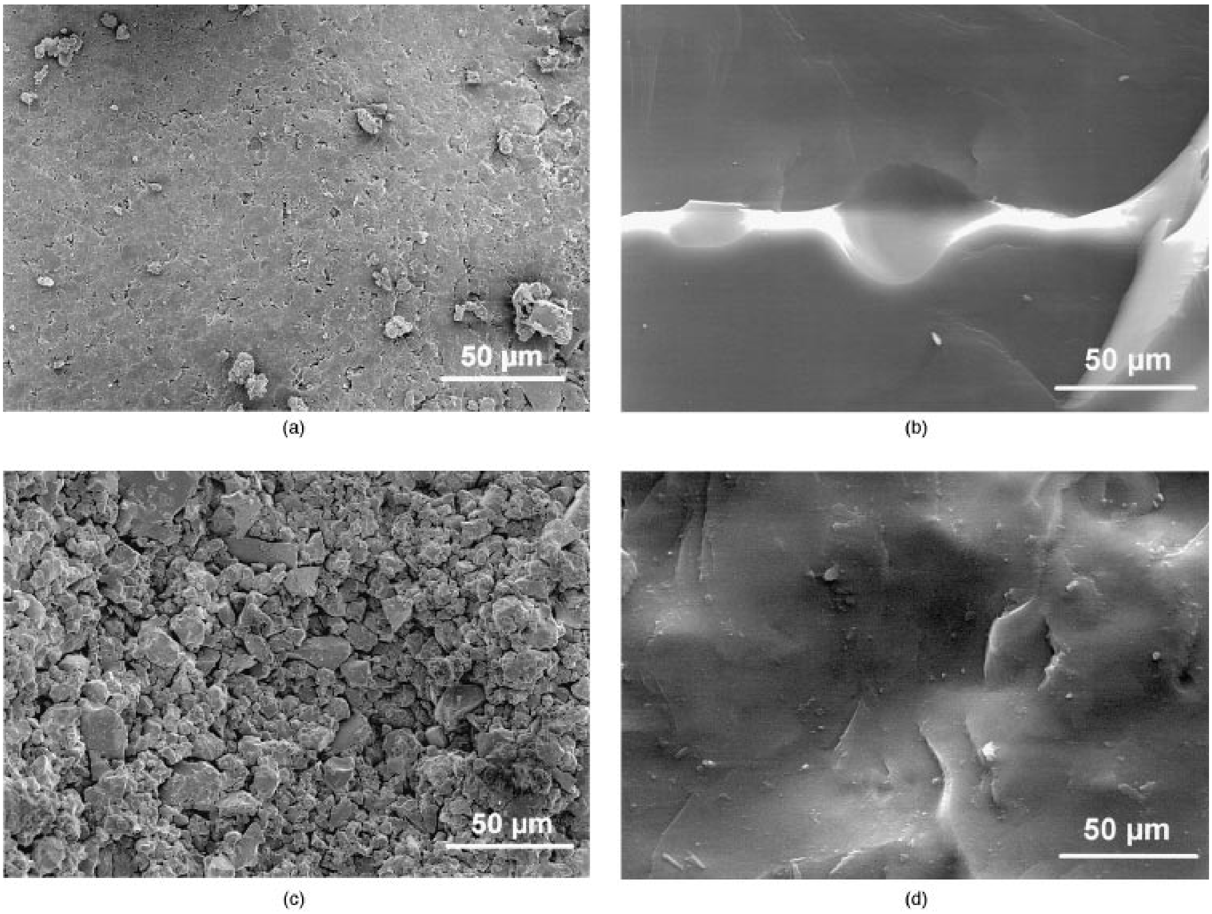

Fig. 4. Micrographs of fracture surfaces of (a) cold and (b) warm pressed polysilazane powders S4 and micrographs of fracture surfaces of amorphous SiCN obtained after pyrolysis of (c) cold and (d) warm pressed samples S4.

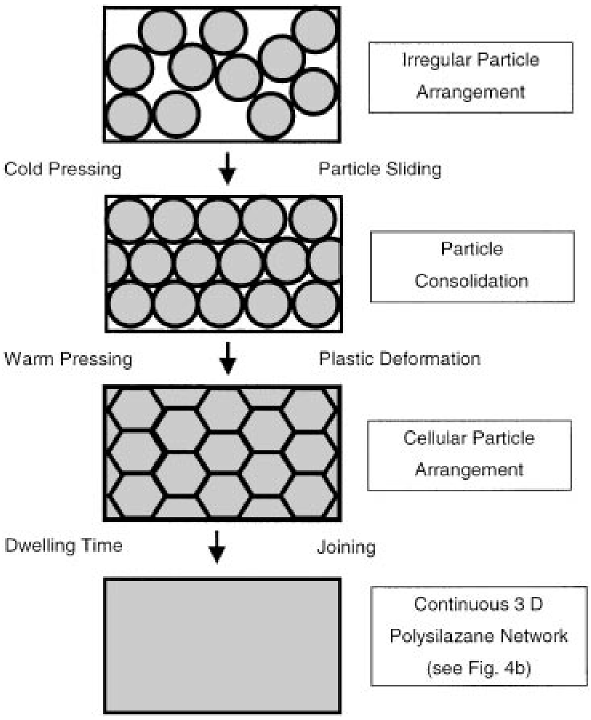

Fig. 5. Proposed densification sequence of cross-linked polysilazane powder during green body preparation at various warm pressing temperatures. During cold pressing particle crushing cannot be excluded.

to a noticeable polymer softening accompanied by simultaneous polycondensation reactions giving off volatile gases like ammonia and methane in the course of pyrolysis. Bloating is not observed in the case of a cold isostatically pressed sample S2 containing a sufficient amount of open pores for complete outgassing of the volatile reaction products. However, no bloating is found during pyrolysis of sample S2 warm pressed at temperatures between 300 and 340°C, although the open porosity of the green body is below 2 vol%. These findings clearly illustrate that warm pressing at elevated temperatures ($\geq$300°C) considerably enhance the degree of cross-linking of the polymer, thus providing an infusible polysilazane matrix required for the formation of dense SiCN ceramics.

Green compacts prepared from powders S2 and S3 by warm pressing at temperatures $\geq$360°C contained significant amount of open pores (11·2 and 17·8 vol%, respectively). After pyrolysis, the porosity of these samples is decreased to 4·3 and 5 vol% and the nanopores are completely eliminated. Therefore, it can be concluded, that nanopores do not seriously hinder densification of the matrix during the polymer to ceramic transformation and can be easily removed. Moreover, the presence of nanopores in green bodies allows for efficient outgassing of volatile reaction products and thus prevents crack formation in the developing ceramic network. The relatively high degree of cross-linking adjusted in sample S3 allowed either cold isostatic or warm pressing without any obvious bloating independent of the temperature applied during the warm pressing procedure.

The pyrolysis of uniaxially cold or warm pressed polysilazane green bodies gave form-stable and crack-free SiCN samples. It is obvious from Fig. 6 that the final ceramic bulk density of the SiCN material strongly depends on the green density adjusted by the warm pressing temperature of the cross-linked polysilazane powders. Cold uniaxial die pressing leads to an open porosity of 23% of the amorphous SiCN material after pyrolysis (S4, 1100°C, 4 h, Ar). Figure 4(c) reveals the corresponding microstructure of a fracture surface of a pyrolyzed uniaxially cold pressed sample (S4, 25°C, 30 min, 710 MPa). The main part of the open porosity is caused due to packing faults between the former polymer particles during the pressing procedure. Warm pressing allows particle deformation and

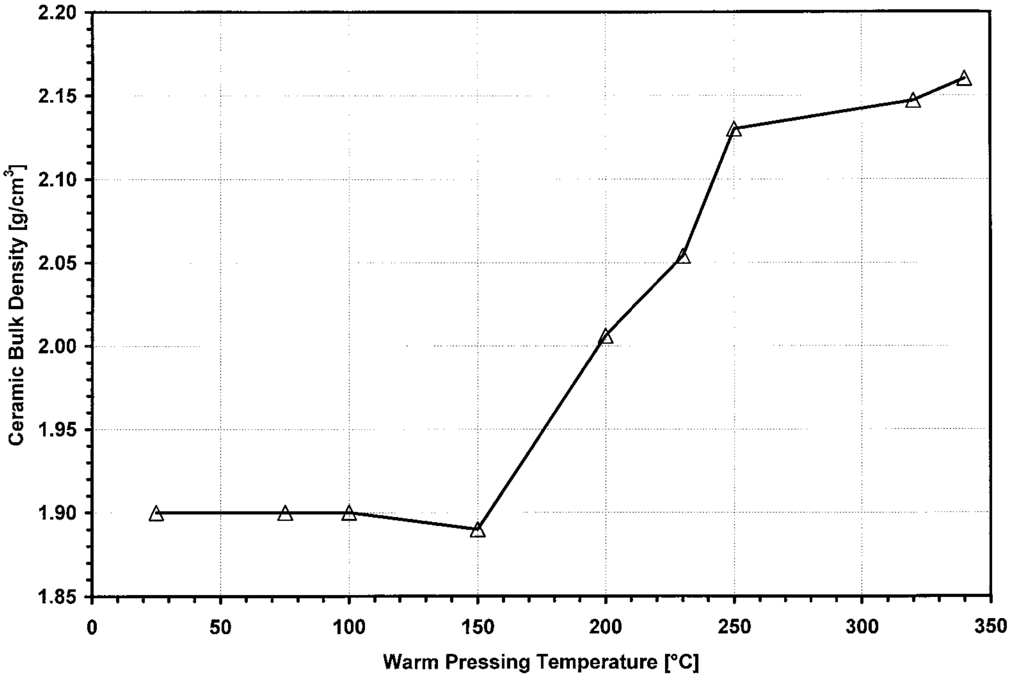

Fig. 6. Development of the bulk density of amorphous SiCN ceramic materials after pyrolysis of polysilazane green bodies uniaxially warm pressed at different temperatures.

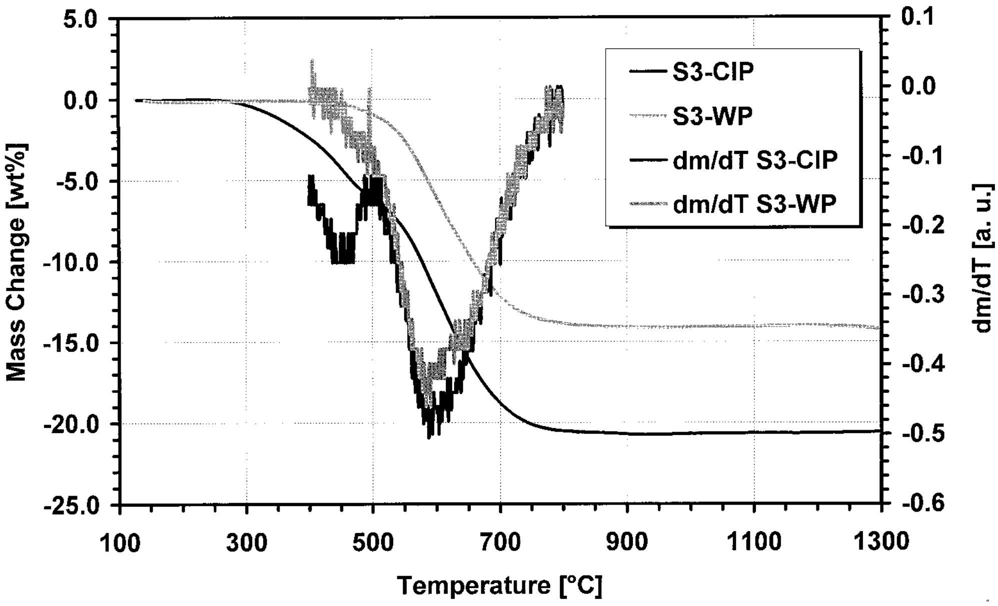

Fig. 7. Thermalgravimetric analysis of samples prepared by cold isostatic (S3-CIP) and uniaxial warm pressing (S3-WP) of cross-linked poly(hydridomethyl)silazane powders. The first derivative (dm/dT) of the thermalgravimetric curves indicate the maxima of weight loss.

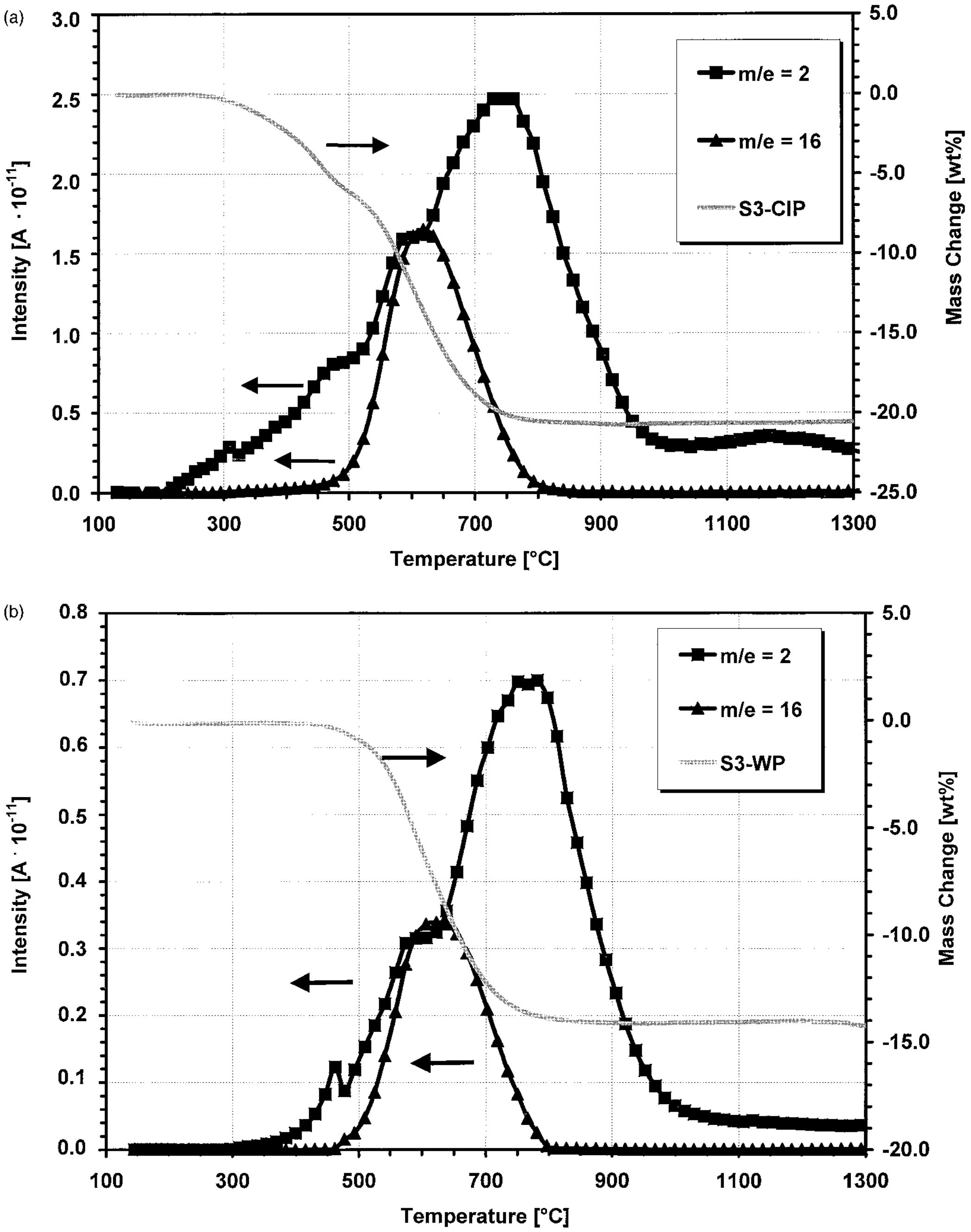

Fig. 8. TGA and ion current curves for hydrogen (m/e = 2) and methane (m/e = 16) detected simultaneously with the thermogravimetric analysis of (a) cold isostatically pressed sample (S3-CIP) and (b) warm pressed counterpart (S3-WP).

particle welding, respectively. An increased green density of as-compacted polysilazane is responsible for a significantly enhanced final bulk density of the amorphous SiCN material obtained after pyrolysis. Figure 4(d) shows a fracture surface of sample S4 uniaxially warm pressed at 340°C for 30 min at 710 MPa subsequently pyrolyzed at 1100°C for 4 h in argon. The open porosity is measured to 1·3 vol%. It is evident from Fig. 4(d) that in the warm pressed samples no cracks and no interconnecting pore system can be identified within the amorphous Si–C–N network after ceramization.

The elemental composition of the synthesized silicon carbonitride ceramics can be described by the general formula $Si_{3+x}C_{x+y}N_4$. The composition is non-stoichiometric in terms of the thermodynamically stable phases, namely Si_3N_4 and x SiC, and formally contains y mole excess carbon. A molar composition of $Si_{3+x}C_{x+y}N_4$ with x = 1·47 and y = 0·88 for the cold pressed samples and x = 1·47 and y = 1·86 for the warm pressed specimens is derived by analysis of the carbon and nitrogen contents. It is worth to note that the formal Si_3N_4/SiC ratio is independent of the applied pressing method while the content of excess carbon is considerably increased by the warm pressing route.

Figure 7 compares the thermalgravimetric analysis of cold isostatically and warm pressed sample 3.

The significant difference in the thermal behaviour up to 750°C is elucidated by the first derivative of the respective TG-curves shown in Fig. 7. While the cold isostatically pressed material loses weight in two destinctly separated stages with maxima around 465 and 595°C, the warm pressed sample only reveals a one stage weight loss at 580°C coinciding with the second maximum of the former sample. As can be seen from Fig. 7 the initial weight loss of approximately 5 wt% of the cold pressed sample found below 500°C is passed on over the whole temperature regime up to 1300°C indicating that similar decomposition processes are taking place above 500°C for both samples. This is veryfied by mass spectroscopic evaluation of the outgassing species detected simultaneously with TGA and is shown in Fig. 8(a) and (b). The first stage weight loss at 465°C of the porous cold pressed sample has to be attributed to the evolution of oligomeric species which cannot be detected by mass spectroscopy using capillary coupling. The increased carbon content analyzed for the warm pressed specimen is in accordance with the TGA-MS study and indicates a reduced methane evolution compared to the cold pressed counterpart.

4 Conclusions

In the present study, warm pressing and subsequent pyrolysis of cross-linked poly(hydridomethyl)silazane powders have been investigated to synthesize dense and crack free amorphous bulk SiCN ceramics with the general composition $Si_{3+x}C_{x+y}N_4$. Transient open porosity formed during the polymer to ceramic transformation process allowed the outgassing of reaction by-products, namely methane and hydrogen. The cross-linking and warm pressing schedule have been optimized: (1) to minimize the amount of volatile species evolved during thermolysis and (2) to attain a sufficient amount of intermediate open porosity which can be completely eliminated after the final pyrolysis. It was shown that warm pressing at high loads enhances further cross-linking during compaction which supports the densification of the cross-linked polysilazane powder. The samples are characterized by a significantly lower weight loss during pyrolysis and higher residual carbon contents compared to cold pressed samples. The successful preparation of dense silicon carbonitrides is now utilized to study the physical and chemical properties of this novel class of ceramic materials, which is presently under investigation in our laboratory.

Acknowledgements

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