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Conversion process of chlorine containing polysilanes into silicon carbide

Part II *Crystallization of the inorganic amorphous silicon carbide derived from chlorine containing polysilane*

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The crystallization of pyrolysed chlorine containing polycarbosilanes (PCS) into silicon carbide is suggested to begin at about 1000 °C by X-ray diffraction experiments. The crystallite size and the crystallite amount were also estimated from the X-ray diffraction patterns. Electron spin resonance, nuclear magnetic resonance and Raman-spectroscopy were used to describe the structure of the material. In addition to these methods a combustion method was used to investigate the carbon and the oxygen contents.

1. Introduction

The chlorine containing polysilanes whose advantages, synthesis, crosslinking process and conversion from a silicon organic into an inorganic state were described in part 1 of this series of papers [1] begins to crystallize at about 1000 °C.

This crystallization is the most important step for determining the latter properties of the ceramic material except for the composition of the material. Especially the SiC-modification, the content and distribution of free carbon and the grain size have a great influence on the properties of the final products. Crystallization is a critical process with regard to the manufacture of silicon carbide fibres. Hasegawa [2] and Hasegawa and Okamura [3] have described the destruction of fibres as a result of crystallization. This is due to a separation of free carbon and a subsequent oxidation created by silicon bonded oxygen. This reaction and the rapid growth of silicon carbide crystallites leads to a dramatic decrease of the fibre strength as has been reported by several authors [2–6]. For this reason it is interesting to investigate the dependence of crystallite properties on the applied pyrolysis regime. In any case one needs information about the conditions of crystallization especially about the conditions which are important for the nucleation and crystallite growth.

Such investigations are reported in this paper. X-ray diffraction, (XRD), electron spin resonance (ESR), nuclear magnetic resonance (NMR) and Raman-spectroscopy and also a combustion method were used to obtain information about the dependence of the structure and crystallites on the pyrolysis parameters.

2. Experimental procedure

The preparation method of the samples was the same as that described in part 1 of this series of papers [1]. The synthesized polysilanes were heated up to the temperatures required for the described investigations under an inert atmosphere (argon) in an alumina tube furnace (Severn Furnace Ltd. UK). After cooling in the furnace the samples were ground for ESR and X-ray diffraction investigations. Pieces of the as-synthesized samples were used in the Raman-spectroscopy experiments.

The X-ray diffraction investigations were performed with an Iris HZG 4 (Carl Zeiss) and CuK_α radiation, the ESR investigations used an Ers 200 (ZWG Berlin) and the Raman investigations (514.5 nm Ar^+, 30 mW) a Gdm 1000L spectrometer.

The combustion method was performed in a silica pipe with a Leco analyser RC 412 for carbon and hydrogen. CO_2 and H_2O were detected by an infrared (IR) detector after calibration with a carbon and water standard sample (benzoic acid). The maximum temperature for the measurement was 975 °C which means that only a small part of the silicon carbide bonded carbon was detected. This amount of carbon was isolated by a deconvolution of the measured curves. The water peaks were also separated into two parts which were related to adsorbed water and also to oxidized hydrogen that had been bonded to the amorphous silicon carbide matrix.

Solid state ^{29}Si magic angle spinning (MAS)– NMR measurements were performed with a Bruker MSL 300 (59.627 MHz). Powdered samples were filled into

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a zirconia rotor and measured at a rotation frequency of 7000 Hz.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns in the region of (1 1 1) peak of SiC (3C polytype β) of samples that were heated up at a rate of 10 K min^{-1} to different temperatures without any dwell time. The grain size was roughly estimated from Bragg-peak broadening of the (1 1 1) peak according the formula:

$$L = \frac{0.9\lambda}{\beta \cos \Theta}$$

where L is average crystallite diameter, λ is the wavelength of the X-rays, β is the half width of the X-ray peak and Θ is Bragg angle of the X-ray peak.

The crystallization process starts at about 1000 °C, at which point the first faint and broad X-ray peak was observed. However a temperature of 1200 °C should in fact be taken as the actual start of crystallization as will be shown by NMR spectra later in this paper. The crystallite size of the sample at 1200 °C was estimated to be about 2.5 nm (Figs 2 and 3). This crystallite size is similar to that of pyrolysed non-chlorine containing polycarbosilanes which were described in references [2–5] and is probably related to similar starting conditions of the crystallization process. Even with a long dwell time at this temperature (24 h) no significant crystallite growth was observed as is shown in Fig. 3. The crystallite size increases with the pyrolysis temperature (Fig. 2) but initially only slowly. As observed for samples at 1200, 1300 and 1400 °C no crystallite growth occurs with dwell time. The crystallites, on average, have a size smaller than 3 nm. Only at 1500 °C, for the first time is crystallite growth observed with dwell time. As can be seen in Fig. 3 the average crystallite size grows to about 5 nm. The starting size of crystallites in samples pyrolysed at 1500 °C is about 3 nm and it reaches 5 nm within 4 h at this temperature. However beyond this point a longer dwell time no longer affects the crystallite size (Fig. 4). The activation energy for crystallite growth is probably just enough to produce a slight increase in the crystallites size. When a certain crystallite size is reached, the effect of impurities and other defects becomes dominant and inhibits any further growth of the crystals.

The X-ray diffraction patterns, Figs 1 and 2, show that a crystallite size not greater than about 5 nm is reached at 1600 °C (without dwell time). The crystallite size reaches about 19 nm at 1800 °C. Non-chlorine containing PCS [2–5] shows a comparable crystallite size and a similar behaviour in the crystallite growth at the beginning of the crystallization process. However, the rate of crystallite growth seems to be higher at temperatures above 1500 °C in those materials. The crystallite size of these chlorine-free substances starts at about 2 nm and reaches a size of about 50 nm at 1700 °C. This observed difference could be caused by chlorine impurities (around 1.5 wt%) that are still present in the material to temperatures as high as 1500 °C. This chlorine could stabilize the amorphous state of the silicon carbide and fix the crystalline defects. A more efficient crystallite growth starts above 1600 °C. Within 1 h a crystallite size of about

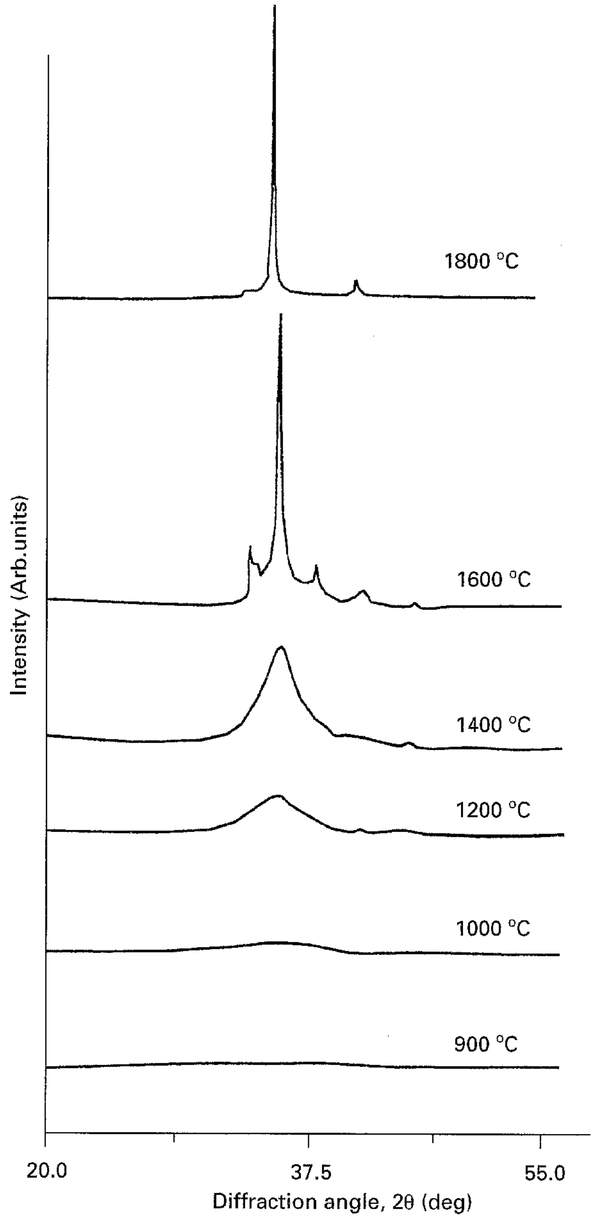

Figure 1 X-ray diffraction patterns of pyrolysed polysilane as a function of temperature.

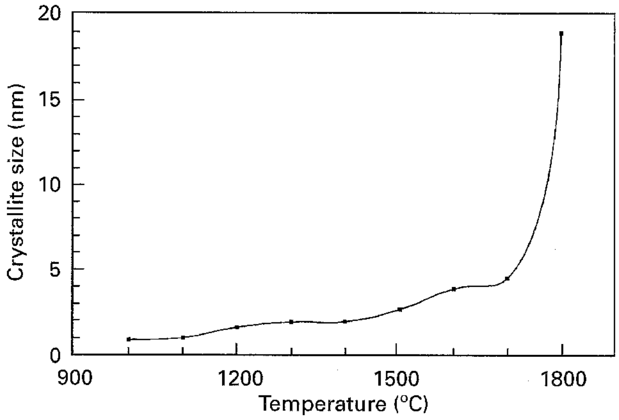

Figure 2 Crystallite size, estimated using the Scherrer formula, versus temperature.

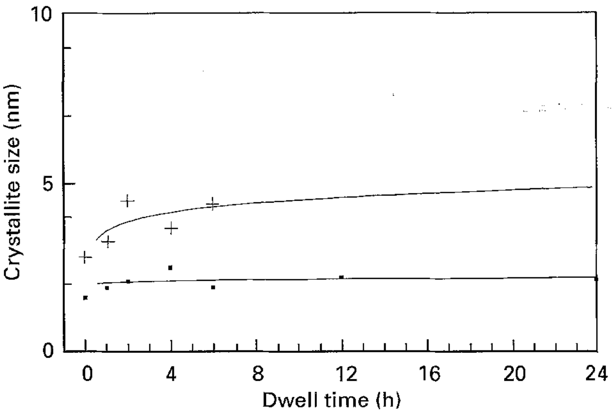

Figure 3 Cyrstallite size versus dwell time at (■) 1200 and (+) 1500 °C.

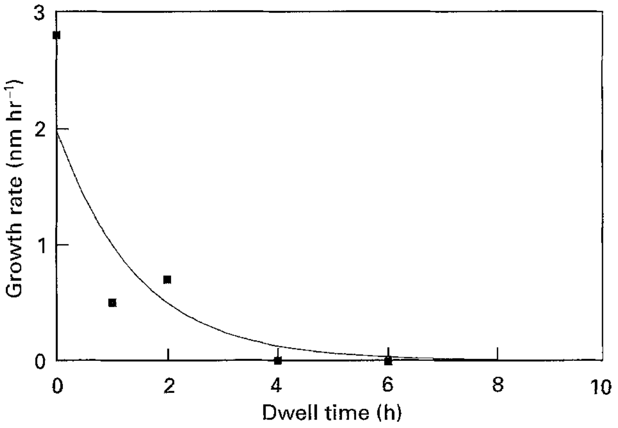

Figure 4 Crystallite growth rate versus time at 1500 °C.

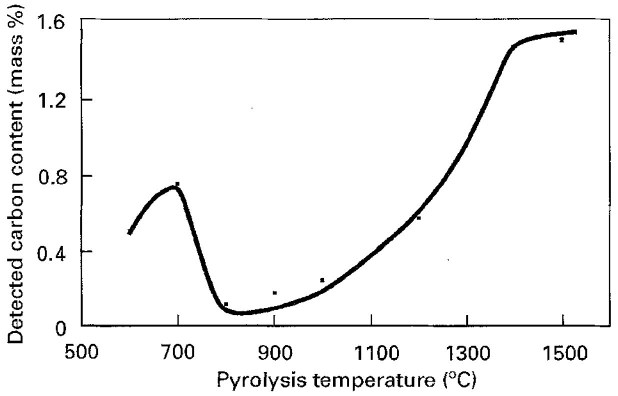

Figure 5 Free carbon in pyrolysed samples versus pyrolysis temperature. The analysis conditions used were 100–975 °C, 20 min heating rate in an oxygen atmosphere.

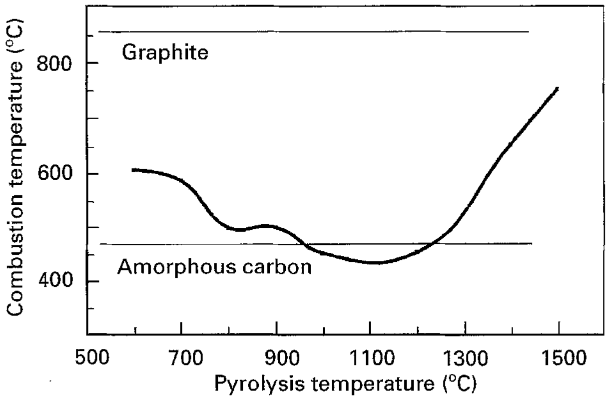

Figure 6 Combustion temperature shift of free carbon in different pyrolysed polysilane samples.

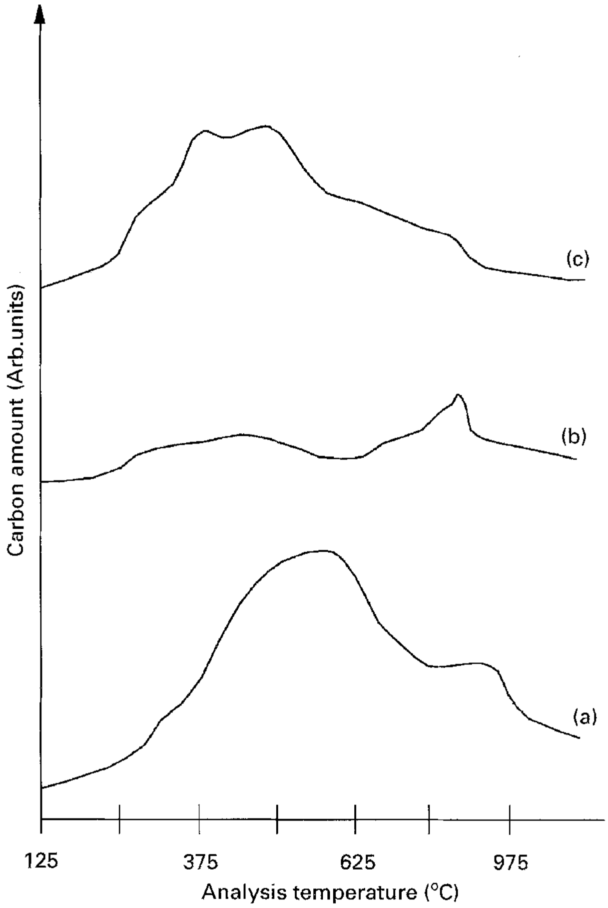

Figure 7 Combustion curves for polysilane samples pyrolysed at (a) 600 °C, (b) 900 °C and (c) 1200 °C.

70 nm is reached. A rapid crystallite growth was observed at temperatures greater than 1700 °C. There is no dwell time required to obtain crystallites of greater than 15 nm size. This is probably due to the removal of the noted impurities as well as to the higher velocity of the atoms which result in the removal of the defects in the crystallite that hindered the formation of large crystallites.

The combustion methods used to characterize the carbon state and structure detected different amounts of carbon depending on the pyrolysis temperature, as is shown in Fig. 5 and the combustion temperature (the temperature necessary to start the oxidation of carbon) in Fig. 6. The analysis of the results of this method has to take into account the following points:

(i) chemical bonding of carbon,
(ii) grain size of the sample,
(iii) other elements contained in the sample.

An example of some typical measured combustion curves are given in Fig. 7. It can be recognized that different fractions of carbon occur that are oxidized at different temperatures. The carbon content in each fraction and the combustion temperature contain information about the points previously listed.

Figs 5 and 6 show that the sample carbon detected from pyrolysis temperatures up to 700 °C burns at

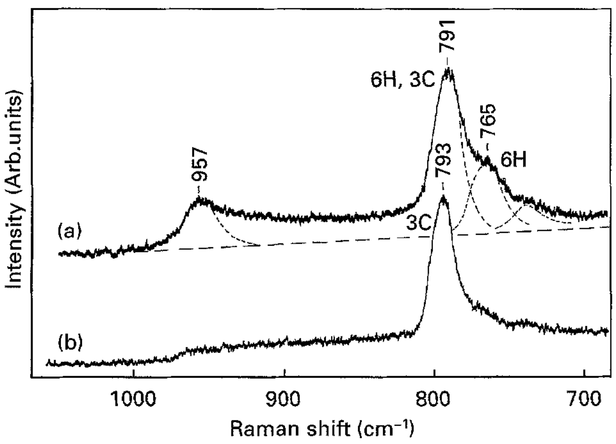

Figure 8 Raman spectra of polysilanes pyrolysed at (a) 1700 °C and (b) 1800 °C.

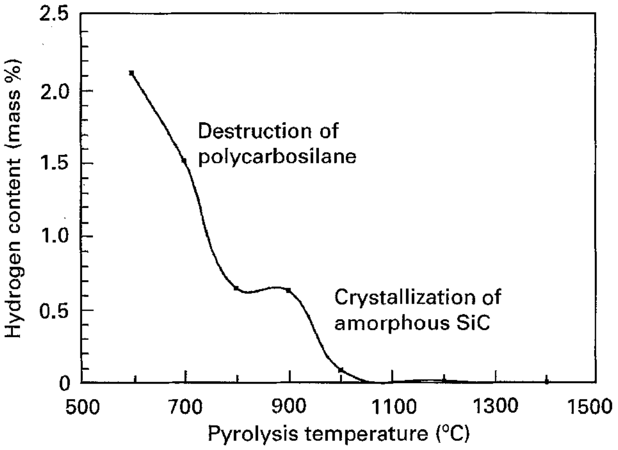

Figure 9 Hydrogen content of polysilanes pyrolysed at various temperatures.

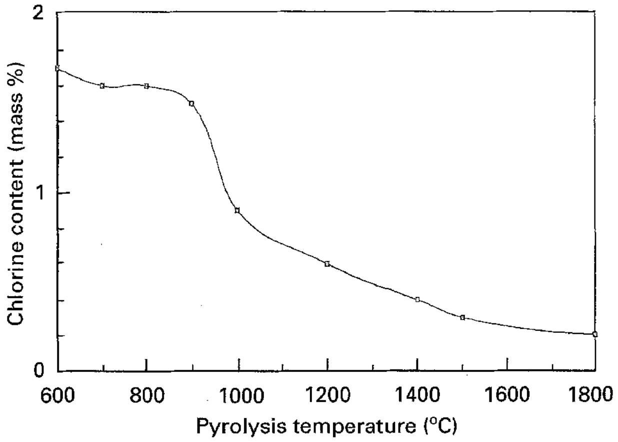

Figure 10 Chlorine content of polysilanes pyrolysed at various temperatures.

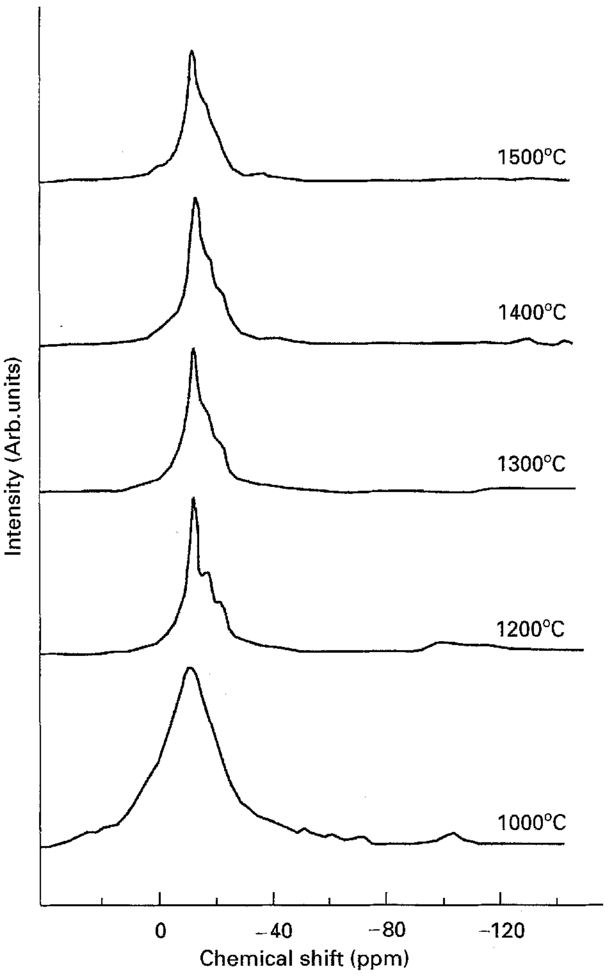

Figure 11 ^{29}Si-NMR spectra of polysilanes pyrolysed at different temperatures.

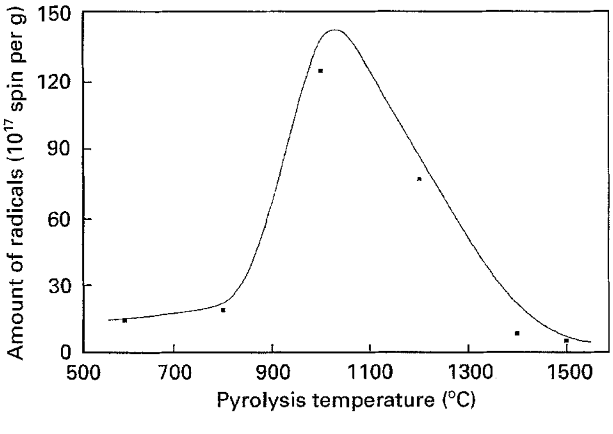

Figure 12 Amount of radicals detected by ESR-spectroscopy as a function of the applied pyrolysis temperature of the polysilane samples.

about 600 °C, and is found at a level between 0.4–0.8 wt%. Samples at higher pyrolysis temperatures (800, 900, 1000 °C) show a much smaller detectable carbon content and a lower combustion temperature. The investigated samples of the next highest temperatures (1100, 1200, 1400 °C) again show an increasing carbon amount and a rising combustion temperature with increasing pyrolysis temperature from 1200–1400 °C.

An explanation for these observations could be that up to 700 °C a polycarbosilane proto-structure is present. This is the reason for a combustion temperature between the combustion temperature of amorphous carbon and graphite (measured on standard samples). Such a polycarbosilane proto-structure is more stable against oxidation than amorphous carbon. Furthermore there should be a self-protecting effect by formation of the amorphous silicon carbide structure during the analysis procedure. However at the beginning of the run at lower combustion temperatures the method detects higher carbon amounts as compared to samples with pyrolysis temperatures of more than 800 °C. The reason for this observation is probably the amorphous structure of the inorganic silicon carbide. The excess carbon is protected by the silicon carbide matrix. Only small amounts of amorphous carbon, which is not included in the Si–C matrix, is combustible in the case of samples derived from a pyrolysis temperature range of 700–1000 °C.

The start of the crystallization process causes the separation of the excess carbon and the production of near stoichiometric silicon carbide. These processes lead to higher amounts of detected carbon and to an increasing combustion temperature. The free carbon is a glassy graphite-like modification [7] as was confirmed by Raman-spectroscopy by bands at 1590 and 1340 cm^{-1} in samples after pyrolysis at 1400 °C (not shown). This carbon covers the silicon carbide particles so that silicon carbide was not found in the Raman-spectroscopy experiments. These indirect observations on the crystallization process are in agreement with the X-ray diffraction results. At higher temperatures, 1700 °C, significant Raman-bands for SiC are found as is shown in Fig. 8.

In addition to these investigations, the hydrogen and chlorine contents were determined. The hydrogen and carbon were measured together with the Leco analyser. The chlorine was determined according to a method described in reference [8]. The sample is oxidized in a flask and the gases were dissolved in deionized water. The chlorine content is simply measured by titration with a NaOH solution. The hydrogen and chlorine data are shown in Figs 9 and 10. As expected at higher temperatures hydrogen and chlorine were detected. These observations show that an amorphous-like state is stable up to high temperatures. Beginning with the crystallization process at around 1000 °C a decrease in the hydrogen and chlorine content is observable (Figs 9 and 10), but the amount of chlorine does not go to zero. It is likely that few amorphous regions still exist at 1500 °C. Even at higher pyrolysis temperatures, a small amount of chlorine was found.

These suggestions are supported by the ^{29}Si-NMR measurements. Fig. 11 shows the spectra of samples after pyrolysis at 1000 °C and 1200 °C respectively. In agreement with the X-ray diffraction investigations a very broad NMR peak is observed for the 1000 °C pyrolysis temperature sample. The long range order of the silicon carbide varies strongly. A completely different "structure" for the silicon carbide is detected in the NMR-spectra of the 1200 °C pyrolysis temperature sample. In this spectra three well defined Si–C carbon sites are detected and only the base of the peak is broadened. The separation of this NMR peak gives intensities at -15, -20 and -23 ppm chemical shift. This seems to be caused by silicon sites of amorphous silicon carbide (chemical shifts in the range between -5 and -18 ppm) and near range structures which belong to β-(chemical shift -18 ppm) and α-polytype structures (chemical shifts around -14, -20, -24 ppm) of SiC. This is evidence of the formation of stacking faults resembling α-polytypes, which can cause associated NMR signals, and they are known to influence the crystallization behaviour as was discussed by Seon *et al.* [9]. Higher pyrolysis temperatures cause a more even NMR peak in the spectra. But this peak, attributed to $\mathrm{SiC_4}$ sites of silicon carbide, is narrower than that of the 1000 °C pyrolysis temperature sample. The lower intensity of additional peaks may be caused by the elimination of crystallite defects and the narrower peak in the spectra by a more organized crystallite structure which is associated with a smaller amount of amorphous material.

The ESR-spectra already discussed in part 1 of this Series of papers [1] shows a maximum in the amount of carbon dangling bonds at a pyrolysis temperature of 1000 °C. On this basis we assume that the most disordered structure exists at this temperature. Obviously this is caused by the cleavage of the hydrogen and chlorine impurities that occurs vigorously in the temperature range between 900–1000 °C as is shown in Figs 9 and 10. The crystallization has just started, as detected by X-ray diffraction, so that almost no elimination of crystallite defects has occured. The progress of the crystallization process results in a decrease in the number of dangling bonds. However they still exist up to a pyrolysis temperature of 1500 °C. This fact provides more evidence that amorphous regions exist even at higher temperatures.

The conversion of the β-polytype (cubic) into the α-polytype (6H) seems to occur on the basis of X-ray diffraction data at temperatures of more than 1400 °C. This process is obviously retarded at temperatures lower than 1600 °C, but it becomes dominant at 1700 °C. However in addition to the 6H-polytype the 4H and 15R-polytypes were also observed in samples pyrolysised at 1500 and 1600 °C. They were characterized by X-ray diffraction peaks at diffraction angles (2θ) of 40.0 and 44.7 °, but these α-SiC-polytypes could not be unequivocally identified by the X-ray patterns (Fig. 1).

Surprisingly, this conversion process was not observed after a pyrolysis temperature of 1800 °C. In addition to the dominant peak attributed to β-SiC, only small amounts of α-silicon carbide were detected by X-ray diffraction and also by Raman-spectroscopy (Fig. 8). Probably, the conversion process is limited to the temperature range between 1500–1700 °C. On the other hand one could doubt the existence of this transformation from β- and α- SiC-polytypes. The Raman spectra should give a more distinguished band for the 6H or other α- SiC-polytypes than that observed. A high level of twinning could create a Raman spectra similar to that shown in Fig. 8. However this explanation is not in agreement with the X-ray and NMR-results. Further investigations are required to completely clarify the situation.

Nevertheless, this behaviour should allow the control of the crystallite structure of the investigated materials. A more detailed description of the polytypes found in these materials will be given in a future paper.

4. Conclusion

The crystallization of β-silicon carbide starts around 1000 °C for organic silicon materials. The crystallite size is similar to the crystallite size reported in previous papers [2–5]. A reason for this observation may be the near stoichiometric ratio of silicon to carbon with a minor amount of chlorine impurities in the investigated polymers after pyrolysis.

The crystallite growth is retarded up to temperatures of 1600 °C. A rapid crystallite growth was observed at higher temperatures. The crystallite amount continuously increases up to 1500 °C. No increase was found at higher temperatures which means that the formation of crystallites is almost complete at 1500 °C.

The state of the carbon changed with pyrolysis temperature. Up to 700 °C the carbon is bonded into a polycarbosilane network. This state is transformed into an inorganic network that can be described as amorphous silicon carbide for pyrolysis temperatures between 700–1000 °C. The separation of carbon (free, glasslike) and stoichiometric silicon carbide (β) is caused by the crystallization process which was observed by means of X-ray diffraction and ^{29}Si-NMR spectroscopy. However this separation process is negligible if the ratio of silicon and carbon is nearly stoichiometric as it was in the investigated polymers.

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