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Crystallization of Polymer Derived Silicon Carbide Materials

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Abstract

Silicon carbide fibres are produced by melt spinning of chlorine containing polysilanes under argon and cross linked by application of ammonia as curing agent and finally pyrolyzed. Their thermal behaviour is investigated. The crystallization process with increasing pyrolysis temperature is characterized by X-ray diffraction (XRD) and small angle X-ray scattering (SAXS). Oxygen, nitrogen and free carbon contents are determined and combined with density measurements in order to obtain information about the microstructure of the system. The comparison of non-cured systems (Si–C) and cured materials (Si–N–C) allows to give an insight into the high-temperature processes. Investigations concerning the nucleation mechanism are further carried out and were described in detail. © *1998 Elsevier Science Limited. All rights reserved*

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1 Introduction

The polymeric route to silicon carbide manufacturing has been extensively investigated during the last 20 years since the pioneering work of Yajima in 1975.[1] The fabrication of silicon carbide or silicon nitride materials has received special attention.[1–3]

Crystallization may degrade the mechanical properties of silicon carbide fibres by altering the original smooth surface. Attempts were carried out to inhibit the crystallization process and to shift it to higher temperatures by incorporation of additional elements such as boron or nitrogen in the starting polymeric precursor.[4,5] In the Yajima process, oxygen was originally used to crosslink the polymer chains in the polycarbosilane fibres.[1] The presence of oxygen has a dramatic effect on the thermal stability of the derived fibres. The degradation process is described elsewhere.[6–11]

A promising way to raise the application temperature is to reach a nanocrystalline structure of the material by controlled crystallization.

The purpose of this paper is to describe the crystallization behaviour of a polymer derived amorphous silicon carbide material. Knowledge of the high temperature processes within the material is crucial for the adjustment of the microstructure in order to improve the material's properties as was recently shown by Monthioux and Delverdier.[12]

In this study the starting polymeric precursor is a chlorine containing polysilane derived from a disilane fraction of the Müller–Rochow synthesis. The synthesis of the polymer was performed by a catalytic redistribution which has already been described in detail in the literature.[13,14] ^{29}Si MAS NMR-spectra of the pyrolyzed Si–N–C samples show the existence of SiC_4 entities (−10 to −20 ppm) and SiC_xN_{4-x} (−25 to −40 ppm) entities that derived from the ammonia curing that has already been published.[15,16]

After pyrolysis at 800°C, X-ray-amorphous Si–C structure is obtained. Its composition is determined by the starting polymer, but contains typically 59 wt% Si, 35 wt% C, 2 wt% H and 4 wt% Cl and some oxygen (< 1 wt%). Some detailed investigations concerning the state of the carbon (amorphous, glassy graphitic or silicon bonded) in

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these pyrolysis products were already published in ref. 17. The conversion process of the polysilane into the amorphous Si–C-material is described in refs. 18 and 19. The ^{29}Si MAS-NMR spectrum of the pyrolyzed precursors shows a broad peak around −12 ppm which is characteristic for an amorphous SiC structure based on SiC_4 sites. The XRD-pattern is essentially consistent with an amorphous structure.

2 Experimental

Si–C and Si–N–C powders were produced by pyrolysis of granulated polychlormethylsilane. The curing process was performed by heating at 220°C under an ammonia/argon mixture in a gas-tight steel container. Then, the powders were encapsulated in a cylindrical carbon vessel and pyrolyzed in a tube furnace in a 99·999% argon atmosphere with a heating rate of 50 K min^{-1} up to final temperature and maintained for 20 min at the temperature before being quenched at high rate. We call this sequence of samples as 'without pre-treatment' (w.p.t.).

Additionally a series of non-cured powder samples (i.e. nitrogen free) were treated as described above and pre-treated at 800°C for various periods of time (3, 4, 6, 8 and 24 h). These specimens were subsequently annealed at 1500°C for 20 min. The mass of such samples were around 1 g, except for the 24 h sample. In order to perform the subsequent crystallization step additionally at 8 and 24 h, apart from 20 min, we produce in this case 3 g of powder materials. This particular kind of preparation was expected to give some information about the nucleation behaviour and the time dependence of the crystallization process. We name the samples produced in this way 'pre-treated' (p.t.).

The annealed samples of both sequences p.t. and w.p.t. were analyzed by XRD with Cu-K_α-radiation. Some selected samples of series w.p.t. were furthermore examined by SAXS. The crystallite size was estimated from the analysis of the profile of the (111) or the (220) reflection of β-SiC (3C-polytype). Density measurements by means of helium pycnometry were carried out in order to obtain more structural information about the specimens.

Samples of series w.p.t. were in addition tested for free carbon, oxygen and nitrogen contents. Oxygen and nitrogen were determined with the LECO analyser (TC 436), the free carbon content was determined using PbO as oxidizing agent for SiC and free Carbon under evolution of CO_2 which is detected barometrically.[20]

3 Results and discussion

The curing-step, necessary for the production of SiC-fibres, leads to an introduction of nitrogen into the system. Hence, the intergranular amorphous phase will be enriched by heteroatoms (N) thus shifted the region of existence of crystallized ceramics to higher temperatures compared to pure Si–C systems, as is described by Monthioux *et al.* In such systems, the formation of the crystalline SiC from an amorphous SiC_x phase is accelerated due to the good chemical compatibility of this matrix-phase which surrounds the crystalline particles.[12]

The results from the w.p.t. sequence, displayed in Figs 1 and 2, are in excellent agreement with the investigations of Monthioux *et al.*[12] In Fig. 1 the development of crystal size with increasing pyrolysis temperature reveals that in both systems the crystal growth mechanism takes place in two steps. The first step, characterized by low growth rates, is followed by a second step with higher growth rates. The beginning of the fast crystal growth depends on the particular system. In the Si–N–C system, the fast growth is shifted to elevated temperatures, around 1400°C, whereas within the Si–C system the fast crystallization starts around 1100°C.

It should be noted that it is absolutely necessary to consider the role of free carbon and of nitrogen as heteroatoms in order to understand completely the crystallization process. In the temperature range between 1100 and 1400°C, the free carbon phase impedes the crystal growth progress by forming a carbon network. The SiC crystals are located temporarily in the cavities of this network like in carbon cages. In this state of conversion crystal growth is only possible by diffusion processes like structural rearrangements or migration

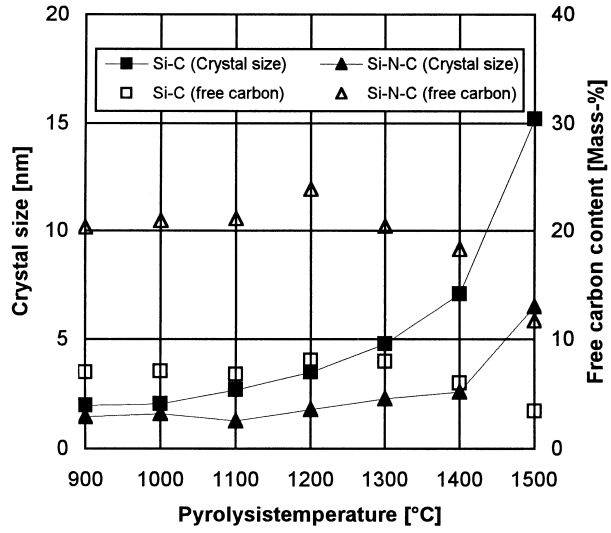

Fig. 1. Crystal size and carbon free fraction for Si–C and Si–N–C as a function of pyrolsis temperature.

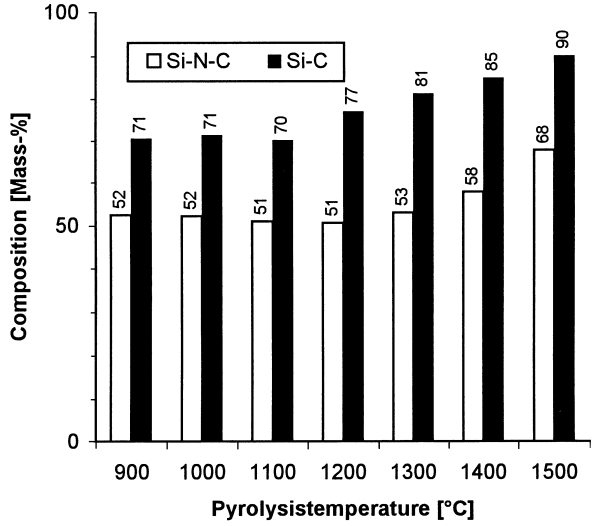

Fig. 2. SiC content for Si–C and Si–N–C systems as a function of pyrolysis temperature.

of defects at the interface of SiC crystals and intergranular phase. This represents the first slow growth step.

At higher temperatures, carbon depletion occurs due to both formation of stoichiometric SiC crystallites and formation of gaseous CO/SiO resulting from oxygen impurities of the starting material or the inert atmosphere.[6] As a consequence, the carbon network will be destroyed, and the crystals can grow very fast by coalescence mechanism.[12] This characterizes the second or fast crystal growth.

The introduction of nitrogen leads to an increase of the free carbon content (Fig. 1) because the formation of Si–N bonds competes with the formation of Si–C bonds in the considered temperature range. These partially occupied Si-atoms are no longer able to form SiC, and this results in a greater excess of carbon. The nitrogen contents are low and the formation of Si_3N_4 was not observed, neither in X-ray patterns nor by Raman spectroscopy. The chemical difference between the intergranular phase and the encircled crystals as well as the increased free carbon content are the main reasons for the slower crystallization of nitrogen containing systems. Hence, the introduction of a heteroatom, like nitrogen, lowers the crystallization tendency in a dual way, although it should be noted that an increase of the free carbon fraction is not beneficial for every application.

The SiC contents as a function of pyrolysis temperature displayed in Fig. 2 provides further evidence for the previous statements. In nitrogen free systems, the SiC content reaches 90 wt% at 1500°C, whereas the SiC content in nitrogen containing systems reaches only nearly 70 wt% at the same pyrolysis temperatures (the difference to 100 wt% results from oxygen impurities and from nitrogen which are located in a $SiC_xN_yO_z$ or SiC_xO_y phase). The reasons for this behaviour are outlined above.

Some selected XRD patterns of the Si–C samples of sequence w.p.t. are shown in Fig. 3. It is obvious that the crystallization proceeds with higher temperatures from the amorphous state at 900°C. The diffraction pattern of the 1500°C sample gives further information about the structure of the formed SiC (the figure represents only a fraction of the measured pattern which ranges from 10 to 100°, 2θ).

The (111)-reflection of the 3C-polytype is disturbed, since there is a disorder-shoulder towards lower diffraction angles and an asymmetrical diffusing shape towards higher diffraction angles. This is typical for one dimensional stacking faults in the cubic structure (along [111]), such as twinning, intrinsic and extrinsic defects. This phenomenon was investigated and described by many authors.[21–23]

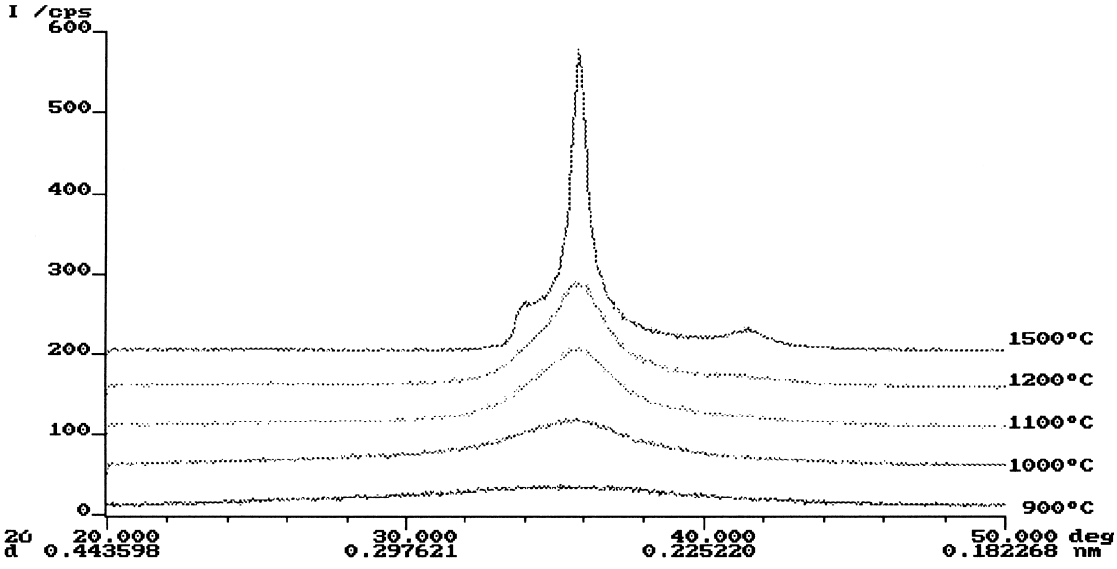

Fig. 3. X-ray diffraction patterns of the w.p.t. sequence, non-cured System Si–C.

Because the (111)-peak is strongly affected by this stacking disorder, the (220)-peak was used for evaluation of the crystal size. It must be mentioned that there is no real 6H-polytype. The real structure can be described as a mixture of various crystallite sizes and disordered regions. In order to describe the disordering and the crystallite size distribution, it is necessary to develop a structure model based on numerical methods like it was recently carried out by Palosz *et al.*[23]

The SAXS investigations were carried out only at five samples of the w.p.t. sequence. The results are presented in Table 1 and Fig. 4. The derived crystallite sizes correspond well with the results from X-ray diffraction displayed in Fig. 1.

In order to investigate the nucleation behaviour samples were pre-treated and then crystallized (series p.t.). This method was applied to glassy systems by many other scientists. In contrary to the presented method, they determined the exothermal DTA signal from the onset of crystallization.[24–26] In this study the assessment of the degree of nucleation was performed by determination of the resulting crystal size obtained in the subsequent crystallization step. High densities of nuclei in the material are favoured in material design because crystallite or grain growth is hindered. Therefore, the final crystal size must be substantially smaller than in the case of a low number of nuclei caused by a low nucleation rate, e.g. if the temperature is too far away from the maximum value of nucleation. The advantage of this more qualitative and indirect determination of the nucleation rate is that it can be carried out by means of relatively simple methods.

It must be explicitly mentioned that influence of the nucleation requires the existence of a temperature range at which the amorphous inorganic state is stable, e.g. between 700 and 900°C as it was reported by Monthioux.[12] This temperature range must be characterized by structural rearrangements and not by the organic-inorganic conversion. However, it must be considered that the release of hydrogen is not completed in the considered temperature range which may influence the nucleation and crystallization behaviour as it is described by Ting *et al.*[27]

Table 1. Results of SAXS measurements

Si–C	*Crystal size (nm)*
1000	2·1
1500	20–30
Si–N–C	
900	1·1
1000	1·4
1500	~11

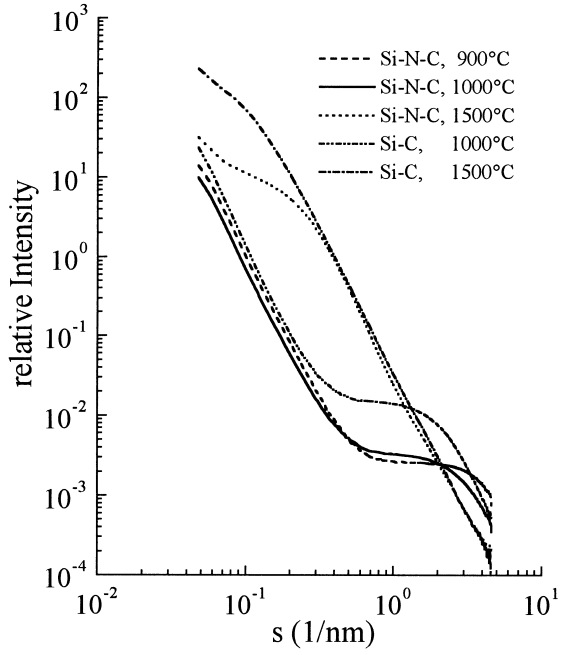

Fig. 4. Relative scattering intensities of SAXS measurements. Results are given in Table 1.

A suitable nucleation temperature is assumed at 800°C because the organic–inorganic transformation is nearly finished as revealed from thermogravimetry,[27,28] except for the release of hydrogen, see above, and the structure is almost X-ray amorphous (see Fig. 5 treatment A). An appropriate crystallization temperature would be 1500°C because crystallization speeds up and there is no larger fraction of amorphous phase visible (see Fig. 3).

Figure 6 shows the dependence of the crystal sizes on the nucleation time at 800°C. Crystal sizes are computed from the annealed specimens (i.e. subsequently treated at 1500°C for 20 min) from peak broadening of the (220)-reflections. Crystallites in the nitrogen containing samples (Si–N–C) are considerable smaller (2–3 nm) compared to nitrogen free Si–C specimen (around 15 nm), which is due to the reasons already outlined.

It is further obvious that nucleation treatments up to 8 h does not significantly influence the crystallite size obtained after subsequent crystallization which is around 15 nm. A dwell time of 24 h results in smaller crystallite sizes of around 7 nm. Probably, the nucleation rate at 800°C is relatively low, and therefore a long period of time is necessary to generate a considerable number of initial nuclei which lowers the final crystal size.

Obviously, the nucleation leads to the formation of an interphase which enriches impurities or heteroatoms (e.g. N, Cl, H, O). This interphase acts as a barrier and hinders further nucleation of SiC because diffusion is slowed down as has been pointed out above. The formation of a considerable number of initial nuclei starts between pre-treatments

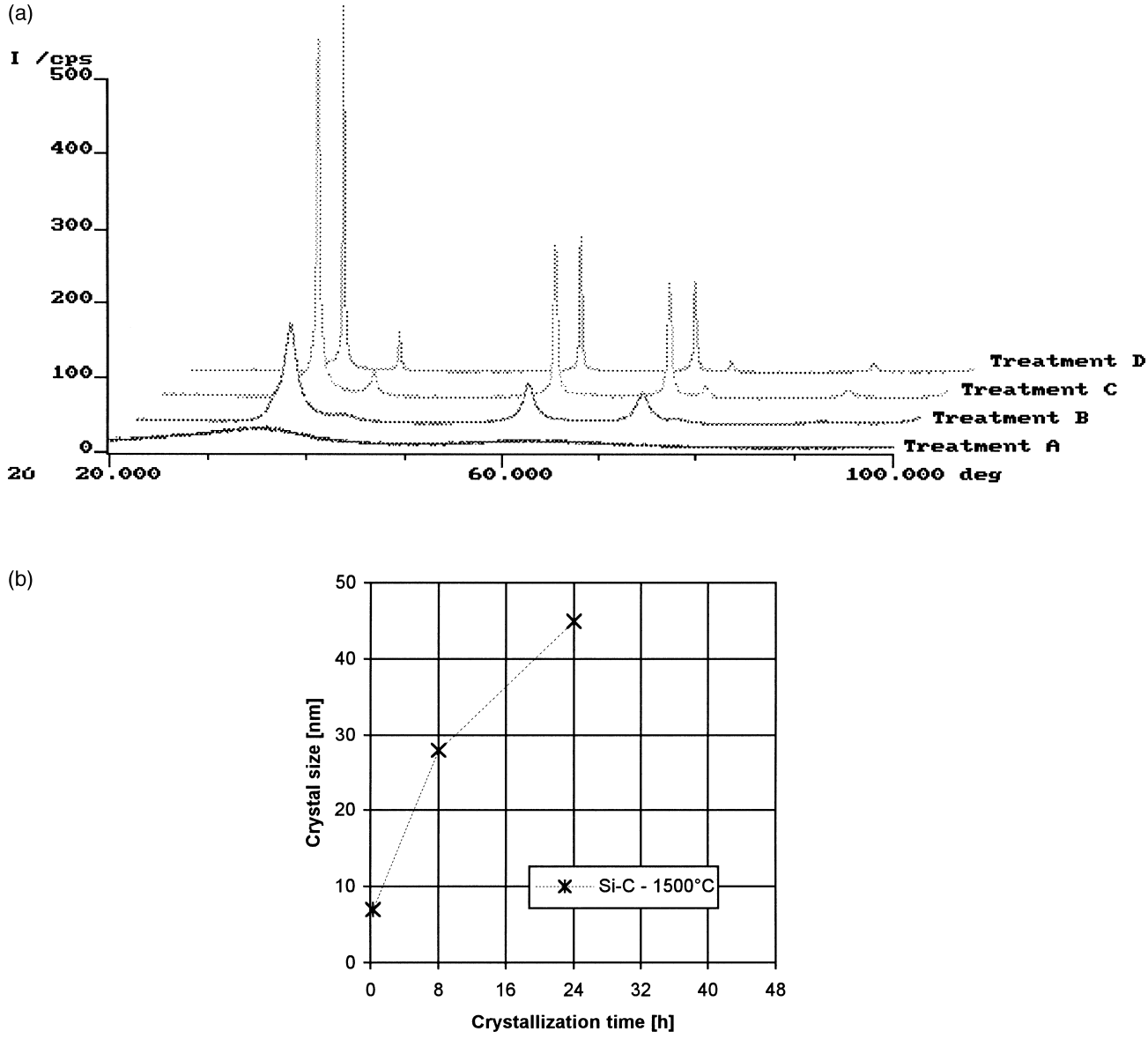

Fig. 5. (a) X-ray diffraction patterns of pre-treated and crystallized nitrogen free samples. (A) after pre-heating at 800°C for 24 h. (B) Sample A with subsequent crystallization at 1500°C for 20 min. (C) Sample A with subsequent crystallization at 1500°C for 8 h. (D) Sample A with subsequent Crystallization at 1500°C for 24 h. (b) Crystal size of the sample pre-treated at 800°C/24 h and after subsequent annealing at 1500°C for 20 min, 8 h and 24 h determined from the XRD pattern in (a).

of 8 and 24 h. This time is called transient time and is described for glass systems by Kelton.[26]

As the nucleation temperature is relatively low, diffusion velocity is slow. The diffusion barrier, formed by the described process, is very effective at this stage of conversion and strongly hampers generation and growth of new nuclei. In addition, the spatial expansion of this barrier prevents the formation of initial nuclei close to each other. That shows that the considered nucleation temperature, i.e. 800°C, is far away from the temperature of maximal nucleation rate. Further experiments are needed and in progress to evaluate the temperature of maximal nucleation rate.

The obtained nanocrystalline structure still changes at elevated temperatures. X-ray diffraction patterns of the Si–C specimens, which were pre-treated at 800°C for 24 h and subsequently isothermally annealed at 1500°C for various periods of time (20 min, 8 and 24 h) exhibits peak sharpening [see Fig. 5(a)]. That indicates crystallite growth with increasing annealing time. Figure 5(b) displays the results of crystal size evaluation from peak broadening. It is obvious, that crystallization proceeds and equilibrium has not been reached during the 24 h annealing treatment. Nevertheless crystal growth rate decreases with increasing treatment time and it is assumed that the crystal size will asymptotically approximate a fixed value. This mere assumption must, of course, be confirmed with further experiments.

Density measurements, carried out with He-pycnometry, of the 24 h crystallized sample results in a value of 3·22 g cm^{-3}, indicating only a small amount of free carbon (1·4% from LECO analyzer) present in the sample, i.e. the sample consists

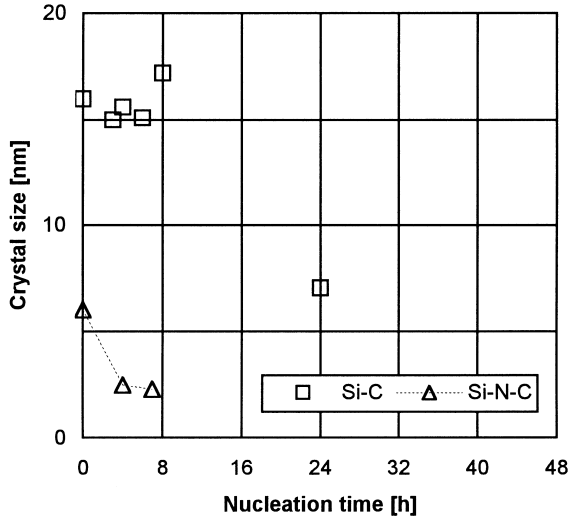

Fig. 6. Crystal size of sequence p.t. after nucleation at 800°C for different periods of time and subsequent crystallization at 1500°C/20 min from XRD.

of nearly pure silicon carbide. The crystallization process is no longer hindered neither by a carbon network nor by an intergranular amorphous SiC_x-phase (nitrogen free system is considered). The density of the X-ray amorphous sample (pre-treated at 800°C) is 2·3 g cm^{-3}. That means that crystallization results as usual to a compaction of the system. Moreover, it is not to exclude that each temperature is characterized by a typical density which has to be confirmed by further investigations.

4 Conclusion

Crystallization and nucleation processes in the Si–C and Si–N–C systems were examined. It has been shown that the introduction of nitrogen leads to a shift of the crystallization process to higher temperatures because an intergranular phase, which is not similar to SiC, impedes the crystal growth. This was verified by evaluating the crystal size from X-ray diffraction experiments and the SiC-content, which is lower in case of the Si–N–C system than in the case of the Si–C system.

Experiments in the Si–C system were carried out with regard to the nucleation mechanism. It is clearly shown that the considered temperature (800°C) is too low to generate a large number of nuclei in an appropriate time. Only long nucleation periods lead to the formation of a considerable number of nuclei, which was quantified by means of the crystal size of the subsequently annealed samples. It can be assumed that, at this stage of pyrolysis, the conversion from organic to inorganic state is already finished. But there is a significant release of hydrogen, and obviously this results to an edge to edge linkage of basic structural units of carbon ('BSU') resulting in the formation of regions which are stoichiometrically more similar to SiC and therefore the nucleation probability in these regions increases which is connected with an increased number of initial nuclei which are able to grow. Furthermore the hydrogen release leads to a structural improvement of the network of excess carbon, which lowers the crystallization. Both effects cause a reduction of crystal sizes. Further investigations must clarify which of both these effects is mainly responsible for the inhibition or deceleration of crystal growth.

X-ray experiments and SAXS measurements corresponds well with the determination of particle sizes. Density measurements support the theory that the amorphous network is densified with increasing pyrolysis temperature until finally the nitrogen free sample pyrolyzed at 1500°C for 24 h contains no considerable amount of amorphous phase.

It is desirable to determine growth rates from the volume fraction which is converted from amorphous to crystalline state depending on the pyrolysis temperature. This is possible with special XRD techniques and will be carried out in the future.

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