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Growth of Amorphous Domains in Precursor Derived Si-C-N-Ceramics Studied with Small Angle X-Ray Scattering

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Abstract. Amorphous precursor derived ceramics with the composition $Si_{26}C_{41}N_{33}$ were isothermally annealed at 1500 °C for 5 minutes up to 190 minutes. Two series of measurements were carried out: one at a nitrogen partial pressure of 1 bar and one at a nitrogen partial pressure of 1 mbar. Small angle X-ray scattering was used to determine the diameter of the amorphous domains. The Guinier radius was found to vary from 9.5 Å to 13 Å irrespective of the partial pressure of nitrogen. This finding is quite surprising since crystallization of this material strongly depends on the partial pressure of nitrogen.

1 Introduction

Amorphous ceramic solids of the system Si-C-N are prepared by solid state thermolysis of pre-ceramic polymers at temperatures of about 1000 °C [1]. The materials are free of sinter additives and exhibit a good high-temperature stability and oxidation resistance [2] making them attractive for applications in various branches of technology. Therefore, one topic of research is to understand the mechanisms of de-mixing, crystallization and coarsening of such materials.

The ceramic material with the composition $Si_{26}C_{41}N_{33}$ will be denoted as VT50C (see next section). The medium range structure of the VT50C ceramics was already investigated with small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) [3]. As-thermolized VT50C ceramics are separated into two phases [3]. Using contrast variation by isotopic substitution (^{nat}N and ^{15}N) theses phases were identified as amorphous carbon and amorphous Si_3N_4 [3]. Annealing at temperatures above the temperature of thermolysis leads to a coarsening of the amorphous phases. The volume fraction of the carbon phase and the Si_3N_4 phase remains unchanged but the average domain size increases with increasing temperature and increasing annealing time [3].

Annealing at 1500 °C and higher temperatures leads to the formation of micro crystalline Si_3N_4 and nanocrystalline SiC [4]. According to the phase diagram of the system Si-C-N (Fig. 1) carbon and Si_3N_4 are in equilibrium at a nitrogen partial pressure of 1 bar and at temperatures below 1484 °C. At higher temperatures Si_3N_4 reacts with carbon and SiC and gaseous nitrogen are formed according to the reaction

$$Si_3N_4 + 3C \rightleftharpoons 3SiC + 2N_2. \qquad (1)$$

This reaction and therefore the micro structure of the ceramic strongly depends on temperature and on the nitrogen partial pressure.

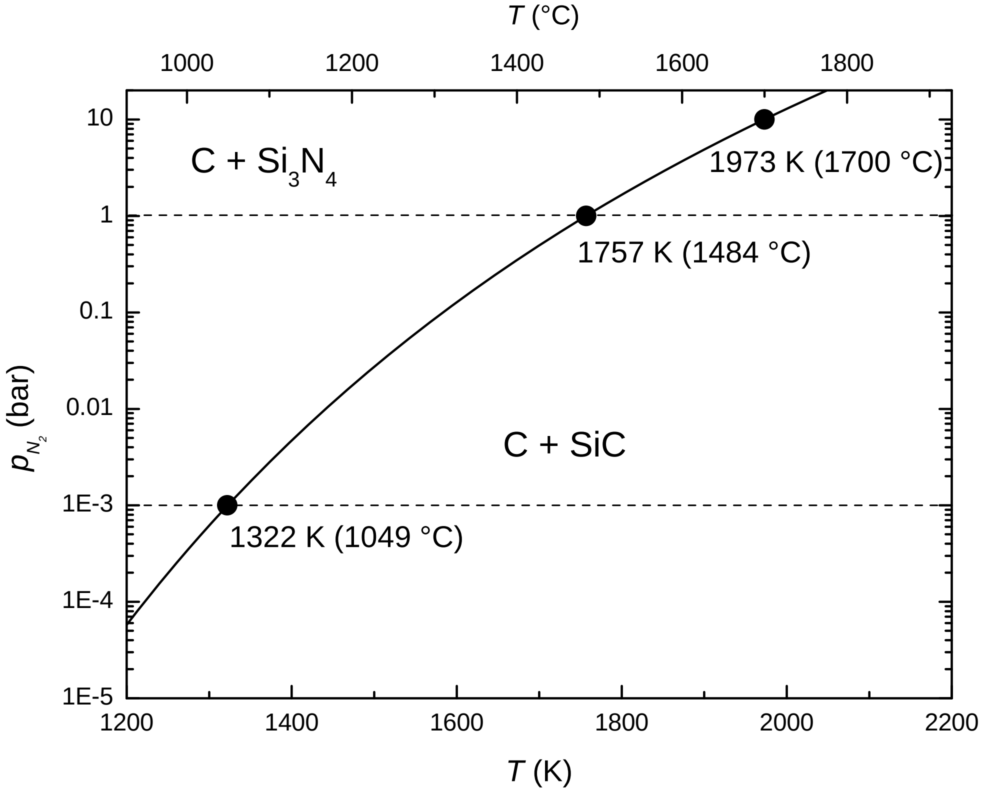

Fig. 1: Phase diagram of the VT50C ceramics after ref. [5]. Indicated are the nitrogen partial pressures used in this work as dashed lines.

Investigations of the crystallization kinetics using X-ray diffractometry (XRD) [4] yielded that Si_3N_4 has a higher stability in the VT50C ceramics than expected from the phase diagram. Annealing at 1500 °C at 1 bar N_2 leads to the formation of micro crystalline α-Si_3N_4. No crystalline SiC was found under these conditions [4]. At higher temperatures additionally to α-Si_3N_4 nanocrystalline SiC is formed at a nitrogen partial pressure of 1 bar and at 1645 °C only nanocrystalline SiC is found [4]. These findings gave motivation to crystallization experiments carried out under a reduced nitrogen partial pressure of 1 mbar. At this nitrogen partial pressure only nanocrystalline SiC is found in the XRD spectra [6]. No crystalline Si_3N_4

could be detected in the XRD spectra in the temperature range between 1450 °C and 1700 °C. At 1500 °C the rate of crystallization of SiC in the samples annealed at a nitrogen partial pressure of 1 mbar is markedly higher than the rate of crystallization of Si_3N_4 annealed at a nitrogen partial pressure of 1 bar [6]. These results give rise to the question whether the nitrogen partial pressure influences the structural transformations in the amorphous state which precede the crystallization. Therefore, in this work we investigated samples of VT50C ceramics annealed at 1500 °C at different nitrogen partial pressures (1 bar and 1 mbar) using SAXS. From the SAXS spectra the radius of gyration, the so called Guinier radius, can be obtained which is a measure of the effective diameter of the domains [7]. Using the results of Dürr *et al.* [3,8] Guinier radii in the range of 5 Å to 25 Å can be attributed to domains of amorphous carbon and amorphous Si_3N_4. We annealed our samples subsequently at the different nitrogen partial pressures and determined the Guinier radii as a function of annealing time. We proceeded annealing until crystallization set in.

2 Experimental

The bulk samples under investigation were produced by isostatic pressing and subsequent thermolysis of cross-linked pre-ceramic polymers at 1050 °C in an argon atmosphere. The polyvinylsilazane VT50 (Hoechst AG, Germany) was used to synthesize amorphous ceramics with a porosity of about 5 %. A detailed description of the preparation procedure can be found in ref. [9]. The composition was determined by chemical analysis to be approximately $Si_{26}C_{41}N_{33}$. Substantial amounts of oxygen (about 2 at. %) and hydrogen (about 5 at. %) are also present. To obtain defined conditions for SAXS investigations the bulk samples were cut into platelets of about $8 \times 8 \times 0.3$ mm^3, polished with diamond paste (particle size: 15 μm, 6 μm, 3 μm, and 1 μm) and cleaned with ethanol in an ultrasonic bath.

To facilitate short annealing times a special mechanical transfer unit was used to place the samples into the hot zone of the furnace within about 2 minutes. The transfer time was neglected. The samples were placed in a crucible and embedded in powder of the same material to protect them from contamination. One type of sample was annealed in a nitrogen atmosphere of 1 bar, a second type of sample was annealed in a mixture of argon and nitrogen with a nitrogen partial pressure of 1 mbar. The annealing temperature was 1500 °C and the time steps were equal for both samples. The total annealing time was 190 minutes. After each annealing step a XRD spectrum was measured with a Bruker D5000 Kristalloflex to ensure that the samples were still X-ray amorphous. SAXS experiments were carried out under room temperature in a Bruker D8 system, equipped with 3D GADDS detector. For the measurements, Cu K_α radiation (λ = 1.541 Å, U = 40 kV, I = 50 mA) was used. Image taken by the detector was integrated over the azimuthal angle in order to get the q-dependence of intensity. Data correction was done by dividing the measured SAXS spectra by the transmission coefficient and subtracting the background. The linear absorption coefficient was calculated using a density of 1.84 g/cm^3 [3] and the atomic absorption coefficients from ref. [10].

3 Results and Discussion

With our experimental equipment we can measure q-values between about 0.1 Å^{-1} and 0.6 Å^{-1} ($q = 4\pi/\lambda \sin(\Theta)$, λ is the wavelength of the X-rays, Θ is the scattering angle). For q-values markedly smaller than 0.1 Å^{-1} the spectra cannot be separated from the background. For q-values larger than 0.6 Å^{-1} the spectra are superposed by the surface scattering of the amorphous domains. Therefore, no integral information could be extracted from the spectra and our analysis was restricted to the evaluation of the Guinier radius.

Fig. 2 shows the Guinier representation of SAXS spectra for VT50C samples annealed at 1500 °C at a nitrogen partial pressure of 1 bar and 1 mbar, respectively. From the slopes of the straight lines fitted to the spectra the Guinier radius, R_g, can be obtained. R_g is the radius of gyration of the largest particle if $qR_g < 1$ holds. As can be seen from Fig. 2 we are at the limit of this condition. For $qR_g > 1$ the Guinier radii can be regarded as an estimate of the particles size. Therefore, the Guinier radii extracted from our spectra can be interpreted as a measure of the sizes of the amorphous domains. According to the results from ref. [3,8] these domains are the amorphous carbon and Si_3N_4 domains. Increase of R_g with increasing annealing time is interpreted due to coarsening of the amorphous domains since the volume fractions of the amorphous carbon phase and the amorphous Si_3N_4 phase remain unchanged [3,8].

After an annealing time of 190 minutes nanocrystalline SiC could be detected in the XRD spectrum of the sample annealed at a nitrogen partial pressure of 1 mbar. The corresponding sample annealed at a nitrogen partial pressure of 1 bar is still X-ray amorphous after an annealing time of 190 minutes in accordance with the findings in ref. [6] where the rate of crystallization for SiC at a nitrogen partial pressure of 1 mbar was found to be higher than the rate of crystallization for Si_3N_4 at a nitrogen partial pressure of 1 bar.

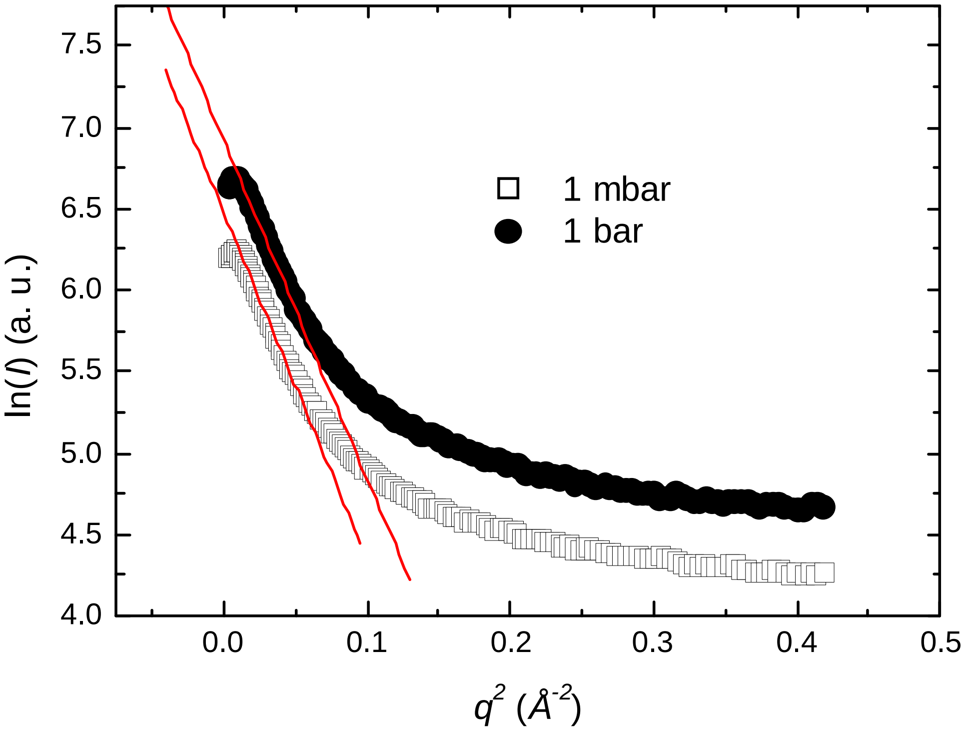

Fig. 2: Guinier representation of the SAXS intensity I for VT50C samples annealed at 1500 °C for 70 minutes at a nitrogen partial pressure of 1bar and 1 mbar, respectively. The upper spectrum was shifted for clarity.

The Guinier radii for the appropriate annealing steps are nearly identical for the different partial pressures. Fig. 3 shows a double logarithmic plot of R_g versus annealing time in which both series of measurements are included. The error bars are the standard deviations of the straight line fits in the Guinier plots. In this representation the data points can be well fitted with straight lines. The fitting parameters are equal within error limits (Table 1) for both series. The empirical result that a straight line fits our data indicates that a power law governs the growth of the amorphous domains in the VT50C ceramics.

Table 1: Intercept *a* and slope *b* of the straight line fits $\ln(R/\text{Å}) = a + b \ln(t/\text{min})$. The errors for *a* and *b* are the standard deviations. From this values *n* and *k* are calculated using eqn. 3. The errors for *n* and *k* are calculated using the error propagation law

Nitrogen partial pressure	intercept *a*	slope *b*	*n*	k (Å^{-n}/min)
1 bar	2.15 ± 0.02	0.077 ± 0.004	13 ± 0.7	$1.4 \times 10^{12} \pm 2.1 \times 10^{12}$
1 mbar	2.14 ± 0.02	0.084 ± 0.005	11.9 ± 0.7	$1.1 \times 10^{12} \pm 1.6 \times 10^{12}$

Grain-growth in crystalline materials can often be described by a generalized grain-growth model [11]:

$$R^n - R_0^n = kt, \tag{2}$$

where R is the radius of a grain at time t, R_0 the initial radius and k a temperature dependent rate constant. The empirical values for n in crystalline materials vary from 2 to 4 [11]. For spherically shaped crystallites diffusion controlled coarsening can be described by the LSW theory developed by Lifshitz , Slyozov [12] and Wagner [13] where $n = 3$. A value of $n = 3$ is found for the coarsening of nanocrystalline SiC in precursor derived amorphous Si-B-C-N-ceramics [14]. These ceramics are quite similar to the ceramics under investigation since the composition of the Si-B-C-N ceramics differs from the composition of the VT50C ceramics only by a small amount of boron. From our data a much higher value for n results which indicates that a different mechanism occurs. If we neglect R_0^n eqn. 2 can be rewritten

$$\log(R) = 1/n \log(k) + 1/n \log(t) = a + b \log(t), \tag{3}$$

which corresponds to a straight line in Fig. 3. From the slope b we can calculate n. The results are included in table 1. The high values for n show that it is justified to neglect R_0 since for an as-thermolyzed sample we find $R_g \approx 5$ Å and for samples annealed at 1500 °C $R_g > 9$ Å which means $R_0^n \ll R^n$.

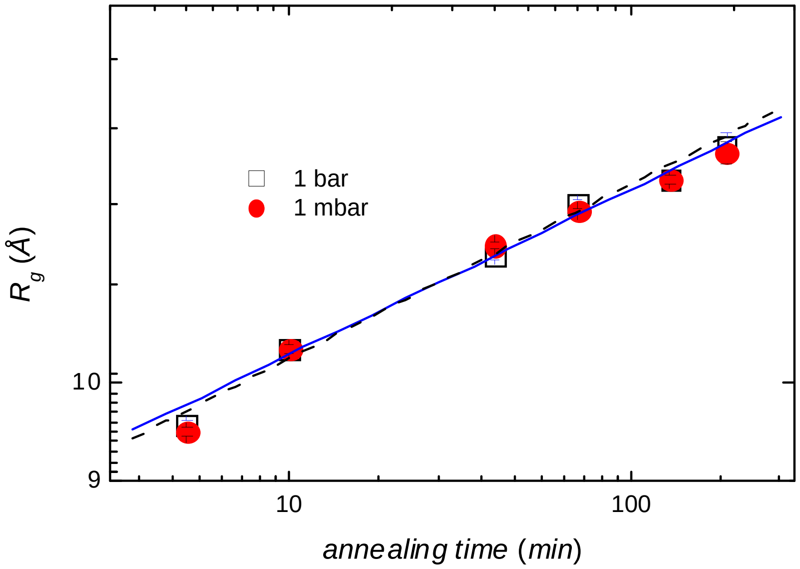

Fig. 3: Double logarithmic plot of R_g versus annealing time t for the samples annealed at a nitrogen partial pressure of 1 bar and 1 mbar, respectively.

From *n* and the intercept *a* in Table 1 the rate constant *k* can be calculated. However, the error of *k* is more than 100 %. This means, that due to the large value of *n* and therefore the large value for the error in *n* the rate constant is not well defined for the amorphous domain growth in our ceramics if eqn. 3 is assumed.

As already mentioned Si_3N_4 is more stable in the VT50C ceramics as expected from the phase diagram in Fig. 1 because only crystalline Si_3N_4 is found at 1500 °C annealed at a nitrogen partial pressure of 1 bar [4]. At a partial pressure of 1 mbar only crystalline SiC and no crystalline Si_3N_4 is found at 1500 °C. This means that the equilibrium of the reaction in eqn. 1 is shifted to higher temperatures for the VT50C ceramics. Since this reaction plays an important role in the crystallization of the VT50C ceramics, crystallization strongly depends on the nitrogen partial pressure. Fig. 3 shows that the Guinier radii do not depend on the nitrogen partial pressure. This means that the nitrogen partial pressure has no influence on the amorphous domain growth at 1500 °C up to annealing times of 190 minutes.

4 Summary

In this study we investigated the growth of amorphous domains in precursor derived ceramics with the composition $Si_{26}C_{41}N_{33}$ using SAXS. The as-thermolized ceramics are separated in domains of amorphous carbon and amorphous Si_3N_4 with an average size of about 5 Å. Since crystallization of the amorphous ceramics strongly depends on the partial pressure of nitrogen two series of measurements were carried out. One sample was annealed at a nitrogen partial pressure of 1 bar and another sample was annealed at a nitrogen partial pressure of 1 mbar. The annealing temperature was 1500 °C. The SAXS spectra were analyzed using the Guinier approximation. In contrast to the crystallization the Guinier radii do not depend on the nitrogen partial pressure within error limits for annealing times from 5 minutes to 190 minutes. In a double logarithmic plot of the Guinier radii versus the annealing time the data can be well fitted with a straight line. Assuming a generalized grain-growth model from the slope of the straight line fits a high exponent $n \approx 12 \ldots 13$ can be obtained. Due to the high value of *n* no reliable value for the rate constant *k* associated with the generalized grain-growth model can be extracted from our data. The mechanism behind the large *n* values is subject of further investigations.

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