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Neutron Diffraction Study of the Amorphous Phase Structure in Silicon Carbonitride Ceramics Obtained by Pyrolysis of a Polyvinylsilazane

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Abstract

The atomic structure of silicon carbonitride ceramics derived from the pyrolysis of a polyvinylsilazane precursor has been studied by means of neutron diffraction. It is shown that the pair correlation function G(r) *of the amorphous phase substituting up to 1400°C exhibits well defined peaks in the medium range order domain along the 0·3–2 nm range. This spectrum can be interpreted as a mixture of siliconcarbonitride phases with an average composition close to* $SiN_{0\cdot98}C_{0\cdot25}O_{0\cdot06}$ *and 1·25 free carbon. The local chemical and structural orders vary continuously in the material from pure aromatic carbon to nanocrystals of* Si_3N_4*, through the ternary SiCN solid solution which is believed to have a structure intermediate between the amorphous and crystalline states.*

In der vorliegenden Arbeit wurde die atomare Struktur von Siliziumkarbonitridkeramiken mit Hilfe der Neutronenbeugung untersucht. Die Herstellung der Keramiken erfolgte mittels Pyrolyse eines Polyvinylsilazanvorläufers. Es wird gezeigt, daß die Paarkorrelationsfunktion G(r) *der 'amorphen' Phase, die bis zu einer Temperatur von 1400°C besteht, wohl definierte Maxima im mittleren Ordnungsdomänengebiet im Bereich zwischen 0·3 und 2 Nanometern aufweist. Dieses Spektrum läßt sich aus einer Mischung aus Siliziumkarbonitridphasen mit einer mittleren Zusammensetzung von* $SiN_{0\cdot98}C_{0\cdot25}O_{0\cdot06}$ *und 1·25 freiem Kohlenstoff interpretieren. Die lokale chemische und strukturelle Ordnung des Materials variiert kontinuierlich von reinem aromatischem Kohlenstoff bis zu* Si_3N_4 *Nanokristallen und geht durch das Gebiet des ternären SiCN Mischkristalls, der wahrscheinlich eine Zwischenstruktur zwischen einem amorphen und einem kristallinen Zustand besitzt.*

La structure atomique des céramiques de type carbonitrure de silicium issues de la pyrolyse d'un précurseur polyvinylsilazane a été étudiée par diffraction des neutrons. La fonction de corrélation de paire G(r) *de la phase amorphe qui subsiste à 1400°C révèle des pics bien définis dans le domaine de l'ordre à moyenne distance (0·3 à 2 nm). Ce spectre peut être interprété comme un mélange de phase carbonitrure de silicium avec une composition moyenne proche de* $SiN_{0\cdot98}C_{0\cdot25}O_{0\cdot06}$ *et de 1·25 carbone libre. L'ordre local chimique et structural varie continuellement dans le matériau d'un carbone aromatique pur à* Si_3N_4 *nanocristallin en passant par une solution solide SiCN ternaire considérée comme étant une structure intermédiaire entre un état amorphe et un état cristallin.*

1 Introduction

Silicon carbonitrides produced from organic precursors have recently been intensively studied as potential candidates in the fabrication of thermostructural composites for applications at high

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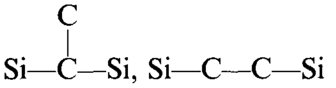
temperature.[1-3] In order to avoid the brittleness at grain boundaries of the polycrystalline state, the molecular structure of the precursor and the pyrolysis process must be optimized in order to prevent crystallization and to preserve an amorphous state up to the working temperature. The retention of the amorphous state at higher temperatures appears to enhance the mechanical properties. It seems that the presence of a free carbon phase increases the crystallization temperature of the material.[4,5]

Microstructural characterization of ceramics derived from polymer pyrolysis has been limited.[6-10] In fact, it has not been shown conclusively whether such materials are microcrystalline or amorphous. This paper describes the structural evolution of ceramic materials obtained at high temperature (1200–1400°C) by neutron diffraction.

The chosen organic precursor in this study is a polyvinylsilazane which is supposed to achieve two objectives: the capability of cross-linking and the precipitation of free carbon during the pyrolysis process.

2 Experimental Procedure

The polysilazane of idealized formula $(\text{–SiViH–HN})_n$ used in this study has already been described.[11] This precursor was prepared by ammonolysis of dichlorovinylsilane in toluene. In order to increase the ceramic yield, the thermal cross-linking of this oligomer prior to pyrolysis is performed. The presence of vinyl and Si–H groups allows fast and efficient thermal cross-linking through the hydrosilation reaction, even at relatively low temperature (120°C). In addition the carbosilane bridges,



$$\text{Si—}\overset{\overset{\text{C}}{|}}{\text{C}}\text{—Si, Si—C—C—Si}$$

formed in this way or by vinyl polyaddition are not affected by the main depolymerization reactions such as the transamination and exchange of Si–N bonds.

During the subsequent pyrolysis under nitrogen, hydrogen and hydrocarbons such as methane, ethylene and propene are released. The corresponding weight loss is about 15%. An elemental analysis of the ceramic pyrolysed at 1400°C, detailed elsewhere,[11] indicates the following composition: $\text{SiN}_{0.98}\text{C}_{1.5}\text{O}_{0.06}\text{H}_{0.06}$ (currently, the hydrogen atoms are usually neglected).

NMR studies[12] of the amorphous silicon carbonitride obtained at 1400°C, revealed that the environments of silicon atoms are mixed tetrahedra $\text{SiN}_x\text{C}_{4-x}$ (x = 0–4). Excess carbon is present as turbostratic carbon. The rate of crystallization of the pyrolysate in Si_3N_4 and SiC was slow. The residues obtained after pyrolysis with a low heating rate (150°C h^{-1}) were compact and microcracked.[13]

The neutron experiment has been performed on the 7C2 spectrometer at the Orphee reactor in the Leon Brillouin laboratory at Saclay (France). This spectrometer has been constructed for amorphous material studies which do not need a good angular resolution. Therefore, this poor resolution serves as a filter, eliminating the narrow lines of the crystalline phases. In our case, the measured diagram is only representative of the amorphous phase and/or nanocrystals having large diffraction lines.

3 Results

3.1 Characteristics of the experimental structure factors

The neutron diffraction spectra of three samples annealed respectively at 1200°C and at 1400°C for 1 h and 6 h under nitrogen are shown in Fig. 1.

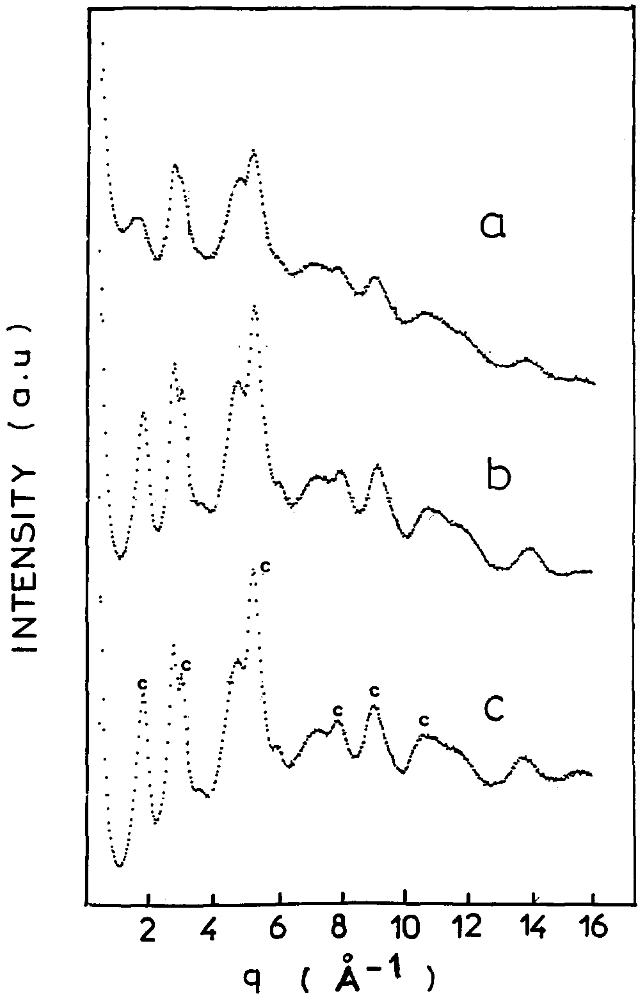


Fig. 1. Experimental neutron diffraction spectra for the three samples annealed at: (a) 1200°C, 1 h; (b) 1400°C, 1 h; (c) 1400°C, 6 h. The diffracted peaks of the turbostratic carbon are marked as C. Note the decreasing effect with temperature of the incoherent scattering of hydrogen.

The diffracted intensities are almost crude results except that the vanadium contribution of the container has been removed from the as delivered data.

The neutron patterns do not exhibit the weak diffraction lines of a small amount of Si_3N_4 crystals as it has been observed on the same sample with a conventional X-ray goniometer.[11] This is due to the poor angular resolution mentioned above.

However, the general aspect of the patterns is more contrasted than the usual profiles of disordered material spectra which exhibit generally a few broad haloes. We have pointed out on the figure the peaks which are expected to belong to the free carbon phase. Note the asymmetry of the peak at 9 $Å^{-1}$ which is characteristic of the two-dimensional morphology of turbostratic carbon.[14]

3.2 Hydrogen content

The first remark which can be made regarding the differences between the three curves (Fig. 1) is concerned with the existence of a 'form factor' $S(q)$ (where $q = 4\Pi \sin \theta/\lambda$) whose scattered intensities decrease with q. This effect is well marked for the sample annealed at 1200°C and is almost cancelled after 6 h at 1400°C.

Its origin is the strong incoherent part of the hydrogen contribution to the structure factor profile. In contrast, due to the nuclear nature of neutron scattering, the coherent scattering cross-section does not have a form factor. The total scattering cross-section σ_{tot} including the incoherent term is tabulated[15] for each element. While the incoherent contribution is usually very weak as compared to the coherent one for most atoms, it is largely predominant in the case of hydrogen ($\sigma_{coh} = 1{\cdot}79$ barns, i.e. 10^{-24} cm^2 and $\sigma_{tot} = 81{\cdot}5$ barns at $q = 0$). In order to calibrate the scattering data of our experiments, we have calculated the theoretical asymptotic value ($q = \infty$) of the total scattering cross-section of 1 mole of the alloy $SiC_{1{\cdot}5}N_{0{\cdot}98}O_{0{\cdot}06}$ excluding the hydrogen content.

$$\begin{aligned} I_\infty &= (\sigma_{Si} + 1{\cdot}5\sigma_C + 0{\cdot}98\sigma_N + 0{\cdot}06\sigma_O)/3{\cdot}54 \\ &= 6{\cdot}26 \text{ barns} \end{aligned}$$

The momentum transfer dependence of the hydrogen incoherent scattering can be easily calculated by using inelastic scattering theory. Moreover, the mean value of the coherent scattering is constant at large q values.

Then, the H content can be easily estimated by trial and error methods. For a given q value an arbitrary proportion of the $S(q)$ intensity is supposed to correspond to the incoherent scattering of hydrogen and a general curve is deduced by taking into account the σ_H form factor. The data are subtracted from $S(q)$. This operation is repeated until $S(q)$ oscillates definitively about a constant value with q.

The subtracted intensity is converted to barns and compared to the tabulated value of σ_H for one atom, yielding directly the H atom number in the alloy formula. The results give respectively for samples (a), (b) and (c) of Fig. 1: 19 at.%, 5 at.% and 0·3 at.%. These values have to be compared with those derived from quantitative proton non-spinning NMR experiments,[12] which are 8·4 at.% and 6·4 at.% for samples annealed at 1200°C and 1400°C for 1 h. There is a severe discrepancy between the results for the first sample that we cannot explain at present.

3.3 Structural changes of heat treated samples

The next point to consider is that the three spectra above $q = 6$ $Å^{-1}$ (Fig. 1) exhibit similar profiles. This means that the local connectivity of the atoms is not drastically modified during the annealing which just enhances the size of the ordered domains. It is well known that the far oscillations of the diffraction patterns of glasses are mainly representative of the short range atomic order in the direct space and vice versa. Indeed, the only significant modification of the spectra with temperature is the sharpening of the peaks at low q which reveals an extension of the medium range order (MRO). For example, the first peak width (Fig. 1) decreases at 1400°C indicating the transition from amorphous carbon to turbostratic carbon layers.

3.4 Pair correlation functions

When the usual correction procedure is made for the experimental data (absorption, polarization, normalization), the structure factor $S(q)$ defined in the reciprocal space is Fourier transformed yielding the Pair Correlation Function $G(r)$ defined in the direct space.[15]

$$G(r) = 1 + \frac{1}{2\Pi^2 \rho_0 r} \int_0^\infty q(S(q) - 1) \sin qr \, dq$$

where ρ_0 is the atomic density of the material.

The resulting $G(r)$ are shown in Fig. 2. The strong peak near 0·5 Å has no physical significance, being generated by an artefact of the Fourier transform procedure.[16] The first actual distance is at 1·41 Å corresponding to close C–C neighbours in amorphous carbon (see Table 1). The intensity of this peak is very strong, indicating the great amount of free carbon. The expected second neighbours between the C–C pairs are also well marked at 2·45 Å.

In order to identify the numerous and strong peaks in the MRO, we have compared in Fig. 3 the first $G(r)$ of the sample treated at 1200°C and the experimental $G(r)$ for the turbostratic carbon[14]

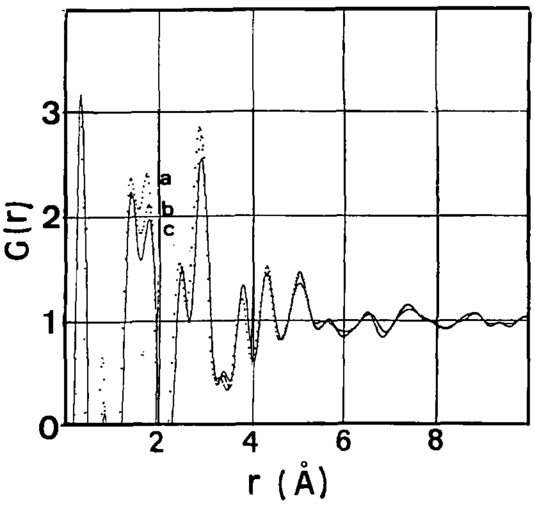


Fig. 2. Pair correlation function $G(r)$ derived from the three $S(q)$ of the samples: (a) 1200°C; (b) 1400°C, 1 h; (c) 1400°C, 6 h. The peak at $r = 0{\cdot}5$ Å is an artefact and has no physical meaning. Note the unusually well resolved peaks for amorphous material in the Medium Range Order domain, between 3 and 6 Å.

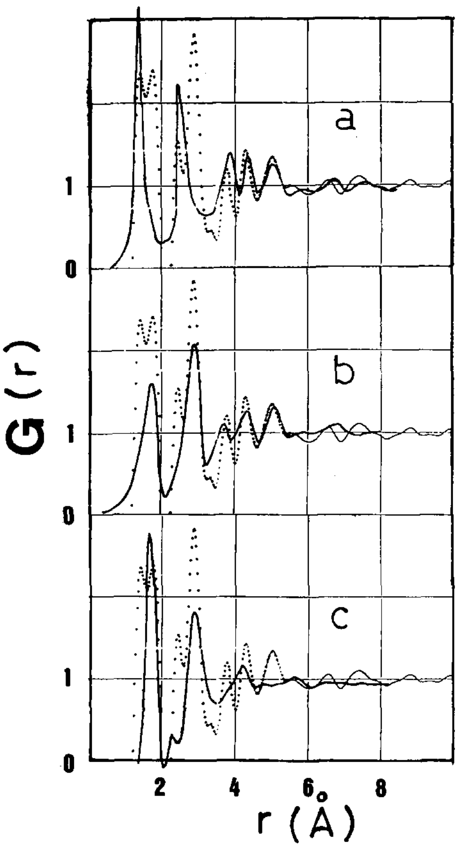


Fig. 3. Comparison between the $G(r)$ of the sample annealed at 1200°C (dotted line), and three different $G(r)$ (continuous line): (a) turbosrtatic carbon; (b) calculated local order in a 28 atoms cluster of crystalline αSi_3N_4; (c) experimental amorphous Si_3N_4. Note that the Medium Range Order peaks are situated at the same place in turbostratic carbon and in crystalline Si_3N_4.

and amorphous Si_3N_4.[17] Moreover, a nanocrystalline $G(r)$ of Si_3N_4 should be also useful. Since there is no experimental example hitherto of this last situation, we have calculated the $G(r)$ of one unit cell of the structure of Si_3N_4 containing 28 atoms. By means of the usual Debye formula

$$S(q) = 1 + \sum_{i\neq j} \frac{\sin (qr_{ij})}{qr_{ij}}$$

for the calculation of powder spectra, the theoretical $S(q)$ has first been calculated using the coordinates given by Ruddlesden and Popper.[18] Then, we have Fourier transformed this function, the integration being limited to the experimental q value of 16 $Å^{-1}$ and after that a Debye–Waller factor $\exp(-Mq^2)$ (M is a constant which depends on the temperature) has been applied to $S(q)$ to simulate the room temperature thermal effects on the curve.

So, the width of the peaks can be compared with both theoretical and experimental pair correlation functions (see Table 1). The first four peaks can be obviously attributed respectively to the short range order in aromatic sp^2 flat hexagons of carbon and in one elementary sp^3 tetrahedron of a covalent silicon nitride. Surprisingly the situation is more confused in the medium range order 3–6 Å (Table 1), where the peaks can be attributed indifferently to pair distances encountered in extended turbostratic layers or in nanocrystals of αSi_3N_4. The simplest model arising to fit $G(r)$ should be a mixture of turbostratic carbon and amorphous Si_3N_4 but we will see below that a fraction of carbon atoms are bonded to silicon. In order to understand this, we have suggested the presence of a silicon carbonitride solid solution in the structural model, having possibly a particular structure different from amorphous Si_3N_4.

3.5 Proportions of bonded and free carbon and the SiCN phase composition

The first neighbour distance of $G(r)$ is the average of all the shortest bonds encountered in the

Table 1. Comparison of the distances in the $G(r)$ shown in Fig. 2.

Distance in G(r)	*Short range order*				*Medium range order*		
Sample annealed at 1200°C, experimental values	1·41	**1·76**	2·45	2·9	3·8	4·28	5·01
Turbostratic C,[14] experimental value	1·42		2·46		3·78	4·25	5·1
Aggregate of 28 atoms in the Si_3N_4 crystalline structure, calculated value		1·74		2·9	3·7	4·34	5·15
Amorphous Si_3N_4,[17] experimental value		1·74		3		4·3 Broad	

material since they are too close to be separated. This average value should be the same, the different types of bonds being regrouped in segregated compounds or spread out in a disordered solid solution. But it has been demonstrated by NMR, as already mentioned, that there was no such segregation.

Moreover, based also on NMR results the C–N, C–O and N–O bonds seem to be absent, thus we consider only Si–N (1·74 Å), Si–O (1·63 Å) and Si–C (1·89 Å) as possible components of the peak at 1·76 Å. Taking into account the increasing Gibbs free energies of formation of Si–O, Si–N, Si–C bonds and the respective valence of elements, 4 for silicon, 3 for nitrogen and 2 for oxygen, we can calculate the average theoretical first distance of the alloy written in the reduced formula: $SiC_{1\cdot5}N_{0\cdot98}O_{0\cdot06}$. In this formula there is one Si which is linked to other atoms in the following manner:

−0·06 at. O saturate 0·03 Si (1 O for 0·5 Si)

−0·98 at. N saturate 0·73 Si (1 N for 0·75 Si)

Hence there is 0·24 atom of Si left to be linked to 0·24 C (1 C for 1 Si). Finally there are in total 1·28 hetero-atoms bonded to 1 Si.

The average distance is then:

$$\frac{1{\cdot}62\times0{\cdot}06+1{\cdot}74\times0{\cdot}98+1{\cdot}89\times0{\cdot}24}{1{\cdot}28}=1{\cdot}763\,\text{Å}$$

This calculated distance is very close to the experimental value (Table 1): 1·763 ± 0·005 Å. A consequence of this result is that (1·5 − 0·24) C atoms are free, i.e. 85% of the total carbon content (37 at. % of the total content). The bonded C atoms represent 0·24/2·28 = 10·5% of the 'amorphous' phase composition, which is $SiC_{0\cdot24}N_{0\cdot98}O_{0\cdot06}$.

In a first approximation, if one neglects the low oxygen content, the SiCN phase composition is almost Si_4N_4C. As far as the local environment of the silicon atoms is concerned, this means that one elementary tetrahedron is, on average, SiN_3C.

4 Discussion

In the framework of the initial goal of increasing the crystallization temperature of ceramics, the most important point to emphasize is the non-evolution of the amorphous phase between 1200 and 1400°C, provided that the annealing is performed in nitrogen atmosphere.

From a crystallographic point of view, the ability of organic precursors to yield SiCN solid solutions at the ultimate scale of an elementary tetrahedron has been achieved. It is worthwhile to recall that despite many efforts in the past to prepare ternary SiCN materials, no crystalline stoichiometric compounds are known up to now in this system, as in the SiNO system, where Si_2N_2O exists.

In the present study, we have seen that on average one neighbour of Si over 4 is a C atom, the 3 others being N atoms. NMR results show that other environments exist such as SiN_2C_2 or SiN_4 so that local compositional fluctuations occur on the disordered network. These fluctuations are promoted by the versatility of the C–C bond which can be involved either in sp^3 or in sp^2 configurations. In the first case, the coordination of C is 4 and the covalent angle is 109·5°. In the second, these values become respectively 3 and 120°, just as they are for N atoms bounded to Si in a Si_3N_4 network.

An alternative model explaining the well defined peaks along the MRO of $G(r)$ should come from the structure of the 'amorphous' phase itself, and the local role played by the substituted C atoms in the close neighbours of Si. EXAFS studies on silicon carbide ceramics[19] has shown that the C–Si–C bond angle is very rigid. In return, the N–Si–N angle is soft (cf. the complex local structure of crystalline αSi_3N_4). Crystalline, SiC $G(r)$ presents a characteristic peak at 3·62 Å which is very weak on Fig. 2. Therefore, a possible model for this particular structure might be a mixture of rigid nodes represented by CSi_4 tetrahedra surrounded by soft NSi_3 linkages. Without long range periodic order as in crystals, the SiCN network stiffened by SiC bonds could nevertheless present well defined peaks in the MRO domain. Above 1400°C, depending on the local C/N ratio, we suggest that the crystallization will be dominated by a kind of percolation process yielding either Si_3N_4 or SiC crystals, while the excess elements should be eliminated in the form of gaseous molecules.

5 Conclusion

The silicon carbonitride ceramic prepared by a pyrolysis of a cross-linked polyvinylsilazane contains 37 at.% of turbostratic free carbon and a $Si_4N_4C(O)$ phase which is not crystallized after 6 h at 1400°C. The local average composition of one tetrahedron within this phase is SiN_3C. The global Pair Correlation Function of the material does not allow conclusions on the actual local order in the SiCN 'amorphous' phase, because of the superposition of the pair distance positions in turbostratic carbon and in crystalline Si_3N_4 in the Medium Range Order domain. Nevertheless, due to the rigidity of C–Si–C bonds, it is suggested that the 'amorphous' phase might be locally more ordered than in amorphous Si_3N_4; this fact could explain the observed resistance against the nucleation and growth of Si_3N_4 and SiC crystals. From a thermodynamic point of view, a local mixed tetrahedron SiN_2C_2 could be envisaged and should correspond to a maximum energy barrier for the long range diffusion process involved in the nucleation of the possible crystalline phases.

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