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A Silicon-29 MAS–NMR Study of α-Silicon Nitride and Amorphous Silicon Oxynitride Fibres

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Abstract

^{29}Si–MAS–NMR with the support of elemental and XRD analyses has been used to assess the structure, the chemical and the phase composition of two types (C and A) of Si–N–(O) fibres prepared according to a gas phase process. The type C fibre consists of α-Si_3N_4 and traces of β-Si_3N_4. It however contains 1–2 at% of oxygen which has been suggested to be distributed within the α-Si_3N_4 structure as a silicon oxynitride. The ^{29}Si–NMR peak at −56·4 ppm may originate from the original Si–N_3O tetrahedral site involved in this structure. The type A fibre consists of a single amorphous silicon oxynitride phase of composition Si–$N_{4(1-x)/3}O_{2x}$. with x = 0·14–0·16 (12–13 at% of oxygen). Silicon atoms in this material are in a tetrahedral environment of statistically distributed O and N atoms (Si–$N_{4-n}O_n$ with n = 0, 1, ..., 4). These different environments give rise to characteristic ^{29}Si–NMR bands, with distinct chemical shifts. Because of the amorphous structure, these bands overlap in the case of the Type A fibre, yielding a single broad NMR band. Their respective intensities and therefore, the shape of the band, are related to the oxygen concentration of the fibre. © *1998 Elsevier Science Limited. All rights reserved*

1 Introduction

Silicon nitride-based materials (Si_3N_4) have been widely studied because of their potential for high temperature engineering applications. Si_3N_4 is indeed characterized by excellent properties in corrosion and creep resistance and high strength at elevated temperatures.[1]

Silicon nitride whiskers and long fibres produced by a gas-phase process have been investigated for many years for metal or ceramic matrix reinforcement purposes.[2,3] Recently, a similar process has been developed involving a high temperature vapor-solid reaction of $SiO_{(g)}$ and $NH_{3(g)}$ on a substrate, yielding long staples of crystalline or amorphous Si–N–O fibres.[4] In preliminary studies, the fibres have been investigated by X-ray powder diffraction to determine the presence of crystalline phases.[5] This technique however fails in identifying and quantifying amorphous structures. Furthermore, elemental analyses of oxygen and nitrogen have been performed to determine the chemical composition, but the molecular fractions cannot be specified by this technique.

The present paper describes, as a complementary technique of the XRD and elemental analysis, the use of Solid-state ^{29}Si nuclear magnetic resonance spectroscopy (NMR), for the chemical and structural analyses of crystalline and amorphous Si–N–(O) fibres. This technique is useful to determine the local coordination number and chemical environment of silicon atoms. The main advantages of ^{29}Si-NMR have been described elsewhere.[6–8] Among others, (i) silicon, silicon nitride, silicon oxynitride and silicates have NMR peaks with characteristic and well defined chemical shifts[6–10] and (ii) this technique is able to quantify accurately crystalline as well as substantial amorphous phase fractions.[8]

2 Experimental

2.1 Fibre synthesis

The fibre synthesis has been described in detail elsewhere.[4] It can be briefly described as follows. About 10 g of a mixture of amorphous silica and titanium (10 wt%) powders was spread on a silicon

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carbide substrate. The powder was then heated up to the processing temperature ($1400 \leq T \leq 1500°C$) and maintained at this temperature during a time t ($4 \leq t \leq 16$ h) under flowing ammonia (10^5 Pa) with a gas flow rate of about $0{\cdot}03\ m\ s^{-1}$. A dense mat of Si–N–(O) fibres grown from the substrate along the gas flow direction was obtained.

The growth of the fibres is achieved through a gas phase process. It involves the reaction of silicon monoxide ($SiO_{(g)}$) and nitriding gaseous species ($NH_{x(g)}$ with $0 \leq x \leq 3$) derived from the decomposition of ammonia at high temperature. $SiO_{(g)}$ is thought to result from the carbothermal reduction of SiO_2 at the silicon carbide-silica interface and/or from the reduction of silica by ammonia.[4] The influence of the synthesis parameters on the properties of the fibres has been discussed elsewhere.[4] Two different processing conditions were investigated in the present study, leading to two distinct types of fibres. The two types of fibres are referred as type A and type C, corresponding to their respective amorphous and crystalline characters.

2.2 Characterization techniques

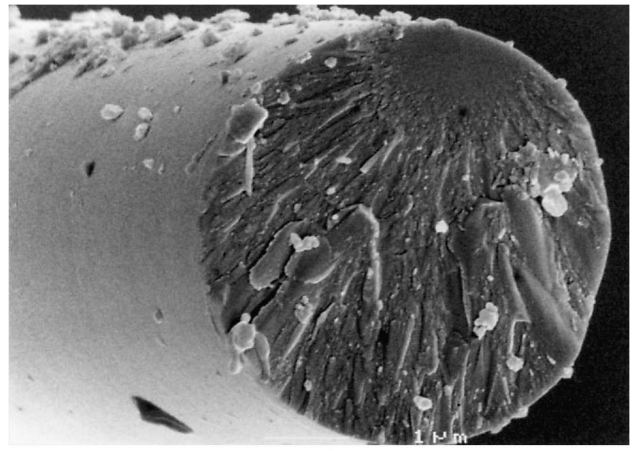
Scanning electron microscopy (SEM) (JSM 6300F from JEOL, Japan) was used to observe the morphology of the fibres. Elemental analyses of oxygen and nitrogen were performed on samples of about 5 mg (TC436 LECO, USA). The average atomic composition was calculated from the O and N weight concentrations after at least five measurements and assuming only the presence of Si, N and O atoms in the fibres. X-ray diffraction (XRD, λCu–K_α) (D500 from Siemens, Germany) patterns were recorded from ground fibres to detect the eventual crystalline phases.

Solid-state ^{29}Si–NMR analyses were performed on the fibres in order to assess the chemical and structural environment of silicon atoms in the material. Single pulse spectra were acquired under the conditions of magic angle spinning (MAS) at room temperature with a resonance frequency of 79·49 MHz (ASX400 from Bruker, Switzerland). The zircon oxide MAS rotor was filled with 300–500 mg of powder and spun at a rate of 5 kHz during acquisition. Crystalline α-Si_3N_4 (SNE-10 from UBE, Japan), Si_2N_2O (research sample) and SiO_2 (α-quartz) samples were also analyzed as standards. The chemical shifts of the ^{29}Si nucleus were externally referenced to tetramethylsilane (TMS). For a quantitative analysis of the different silicon environments in the fibres, the dispersion of the respective spin–lattice relaxation times has to be taken into account.[8] Therefore, two different analysis conditions were used for the fibres. The first one was a single pulse sequence of a tip angle of 15° and a 60 s relaxation delay, whereas the second was a 45° pulse followed by a 10 s relaxation delay. The two sets of parameters resulted in strictly identical spectra. It was thus ensured that the acquiring conditions were compatible with a quantitative analysis of the spectra.

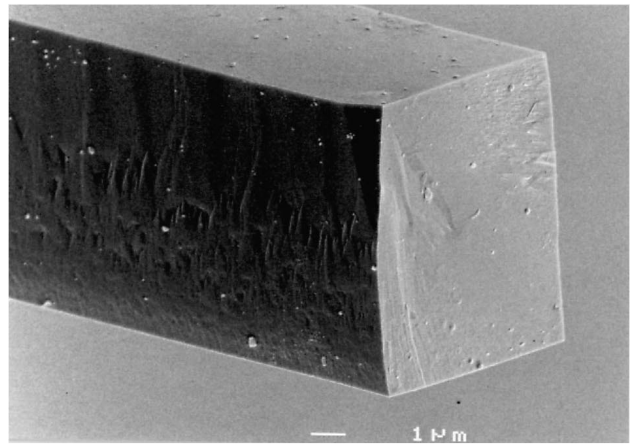
3 Results

3.1 Morphology analyses

Examples of fracture surfaces of the two different types of fibres are shown in Fig. 1. The fibre from type A clearly shows a typical amorphous like material fracture surface, i.e. a mirror surface surrounding the flaw at the origin of failure, itself surrounded by a rougher surface zone [Fig. 1(a)]. The cross section of the type A fibres was always observed to be strictly circular and the surface of these fibres perfectly smooth, without any evidence of a micro-textured material. Conversely, the morphology of the type C fibres is obviously crystalline as shown in [Fig. 1(b)]. The surface of the fibres shows facets generally oriented along the fibre axis and their cross section are polygonal with a



(a)



(b)

Fig. 1. (a) Fracture surface of a type A fibre; (b) fracture surface of a type C fibre.

triangle, square, diamond or hexagonal shape. Compared to type A fibres, their fracture surfaces are smooth, plane or with an eventual step like morphology. Their surfaces show evidence of a faulted crystal structure (e.g. with intergrowth, twinning and polymorphism).

3.2 Chemical analyses

Chemical analyses of the two types of fibres are shown in Table 1. While the fibres from type C have a composition close to that of pure silicon nitride (Si_3N_4), fibres from type A exhibit a significantly higher oxygen concentration (12–13 versus 1–2 at%) corresponding to a composition located between Si_3N_4 and Si_2N_2O (20 at% of oxygen) on the Si–N–O phase diagram. XPS analyses coupled with argon milling revealed a slightly higher oxygen concentration at the surface of the type A fibres but confirmed that the major part of the oxygen is distributed within the bulk.

3.3 XRD analyses

The diffraction patterns of both types of fibres are shown in Fig. 2 and confirm the features described above. Type A fibres show a typical amorphous structure with two very broad peaks. Conversely, type C fibres only show narrow and intense diffraction peaks which are characteristic of a predominant α-Si_3N_4 phase and traces of β-Si_3N_4. A quantitative analysis accounted for an α phase ratio of α-Si_3N_4 of about 98 wt%. No crystalline SiO_2 nor Si_2N_2O phase was detected on the XRD pattern of the both fibres. The crystalline ^{29}Si–NMR standards (α-Si_3N_4 and Si_2N_2O) were also submitted to XRD analysis. The commercial silicon nitride powder consists of only α-Si_3N_4 and traces of β-Si_3N_4 (respectively, 97 and 3 wt%). The spectrum of the Si_2N_2O sample prepared in the laboratory showed the presence of significant amounts of β-Si_3N_4 and to a lesser extent α-Si_3N_4, in addition to crystalline Si_2N_2O.

3.4 MAS ^{29}Si–NMR analyses

The ^{29}Si–NMR spectra of both types of fibres compared to the crystalline standards are shown in Fig. 3. The main results (chemical shifts, full width at half height (FWHH) and peak area ratio) are presented in Table 2. All the crystalline compounds show well defined and narrow resonance peaks. The spectrum of the commercial α-Si_3N_4 powder shows two narrow peaks at −49·0 and −46·9 ppm, with almost the same intensity and FWHH, in good agreement with spectra already presented in the literature for similar materials.[6,8] The spectrum of the Si_2N_2O research sample shows two peaks, an intense one centered at −61·2 ppm and the second

Table 1. Chemical composition of the fibres

	Si (at%)	*N (at%)*	*O (at%)*
Type C fibre	43	55–56	1–2
Type A fibre	41	47–46	12–13

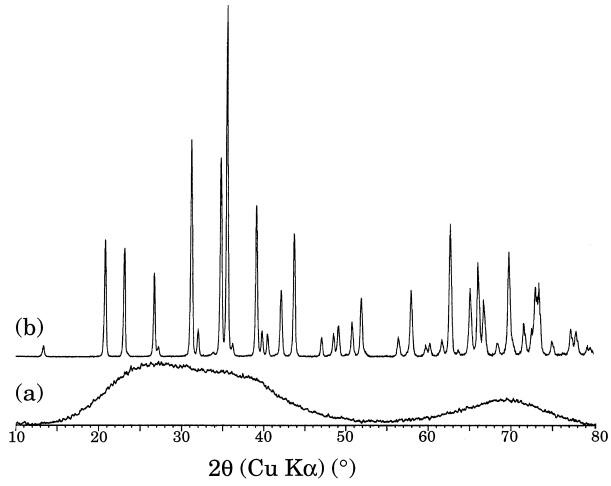


Fig. 2. XRD patterns of the fibres from (a) type A, and (b) type C.

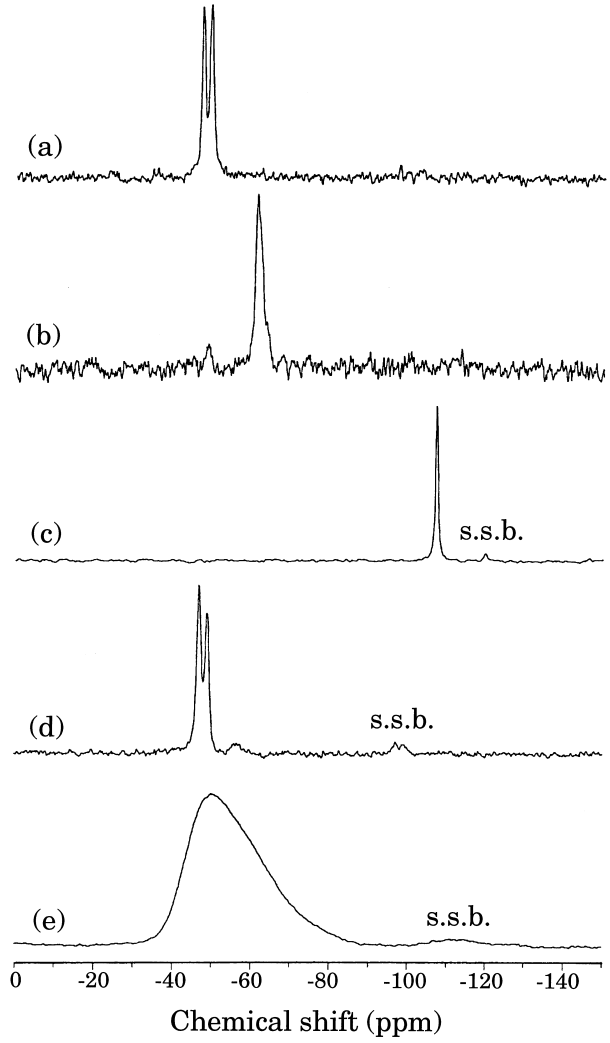


Fig. 3. Silicon-29 MAS–NMR spectra of (a) α-silicon nitride, (b) silicon oxynitride, (c) α-quartz, (d) the type C fibre and (e) the type A fibre. s.s.b. are spinning side bands. The MAS rate was 5 kHz except for (c) where it was only 1 kHz.

Table 2. Spectral parameters for crystalline standards and the fibres

Material	*Peak maxima (±0·2) (ppm)*	*FWHH (±0·2) (ppm)*	*Peak area ratio (%)*
α-Si_3N_4	−46·9	1·1	45
(UBE SNE-10)	−49·0	1·3	55
Si_2N_2O	−48·9	1·8	8
(Research sample)	−61·2	2·2	92
α-Quartz	−107·5	0·9	100
	−46·6	1·3	52
Type C fibres	−48·8	1·5	42
	56·4	3·0	6
Type A fibres	−50·0	21·7	100

one at −48·9 ppm. The former is characteristic of the crystalline Si_2N_2O phase whereas the latter confirms the presence of crystalline Si_3N_4 phases, with a high β-Si_3N_4 phase fraction, as suggested by the single −48·9 ppm peak within the range −50 to −46 ppm.[6,8] This feature has also been pointed out by other authors for the analysis of similar materials.[8] As a matter of fact, synthesized silicon oxynitride powders usually contain significant amounts of silicon nitride owing to the slow kinetics involved in the high temperature solid-state reaction. The spectrum of the quartz sample exhibits a characteristic single narrow peak at −107·5 ppm, as already reported.[9,10]

The ^{29}Si–NMR spectrum of the type C fibres is very similar to that of the α-Si_3N_4 powder, with the same doublet at −48·8 and −46·6 ppm but with slightly different relative intensities. Another interesting feature is the presence of a weak but well defined peak at −56·4 ppm which was not observed in any spectrum of the crystalline standards.

In contrast with all the other crystalline materials, the spectrum of the type A fibres exhibits a single very broad and asymmetric peak from −35 to −85 ppm, along with all the peak positions from the spectra of crystalline Si_3N_4 and Si_2N_2O. Since the spinning side band (s.s.b.) of the main ^{29}Si–NMR peak, observed from −140 to −95 ppm for a spinning rate of 5 kHz (Fig. 3) may interfere with a peak due to the eventual presence of an SiO_2 phase (at about −110 ppm), a further acquisition was made with a lower spinning rate. It was thus insured that no line characteristic of a SiO_2 phase was detectable on the spectrum of the type A fibres.

4 Discussion

4.1 The type C fibres

Fibres from type C were found to be strictly crystalline according to the XRD analysis. Only very sharp peaks corresponding to large crystalline domains (several hundreds of nm) were detected. No broad peaks (e.g. like those visible on the XRD pattern of the type A fibres) characteristic of an amorphous state were observed on the background spectrum. The fibres consist mainly of the α-Si_3N_4 phase and small amounts of the β-Si_3N_4 phase. The latter phase might be located throughout the nanostructure of the fibre as α-Si_3N_4 crystalline defects such as stacking faults, twins or dislocations induced during the fibre growth, as suggested by optical microscopy and SEM analysis [Fig. 1(b)]. It is worthy of note that no crystalline oxygen rich compounds (e.g. SiO_2 or Si_2N_2O) were detected by the XRD analysis. This feature suggests that the 1–2 at% of oxygen could be either present in the fibre in an amorphous material (e.g. silicon oxide or silicon oxynitride) not detectable by XRD analysis, or included within the α-Si_3N_4 structure as already proposed by other authors.[11–16]

The ^{29}Si-NMR spectrum of the fibres from type C agrees with the one obtained for the α-Si_3N_4 reference sample and those presented in the literature.[6,8] Two well separated peaks appear within the range −50 to −46 ppm in spectra of the α-Si_3N_4 based materials owing to the presence of two distinct tetrahedral environments of silicon atoms in this phase (e.g. with small differences in the Si–N bonds length and angles and in the symmetry). Conversely, only one tetrahedral site of silicon atoms exits in the structure of the β-Si_3N_4 phase and gives rise to a single peak at −48·7 ppm in the ^{29}Si–NMR spectrum.[8] The peak area ratios of the latter two peaks slightly differ in the case of the reference sample (α-Si_3N_4 SNE-10) (respectively, 45/55% for the −46·9/−49·0 ppm lines) while they should have similar amplitudes owing to the equivalent occupancy of the two silicon sites. This feature might be due to the presence of significant amounts of β-Si_3N_4 phase in this sample, the resonance line of β-Si_3N_4 (−48·7 ppm from Ref. 8) overlapping with the low frequency line of α-Si_3N_4 (−49·0 ppm).

A weak peak was observed at −56·4 ppm on the ^{29}Si–NMR spectrum of type C fibres in addition of the typical peaks due to crystalline Si_3N_4. This narrow peak, which is well resolved and reproducible, characterizes a crystalline silicon-containing material but is neither consistent with Si–N_4 tetrahedral environment in α or β-Si_3N_4 phases (ranging from −50 to −46 ppm), nor Si–O_4 in crystalline SiO_2 (ranging from −109 to −107 ppm).[9,10] The presence of 1–2 at% of oxygen in the type C fibres suggests that this peak could be more likely assigned to a mixed oxygen–nitrogen environment of silicon atoms in a silicon oxynitride material. The occurrence of crystalline Si_2N_2O, which is the

well known crystalline silicon oxynitride phase, is nevertheless dismissed, firstly by the XRD analysis and secondly because the ^{29}Si–NMR spectrum of the pure Si_2N_2O phase exhibits only one peak at −61·2 ppm, corresponding to the single tetrahedral environment $Si–N_3O$ involved in the structure of the material.[17] Carduner *et al.* have also observed an anomalous band at −57 ppm on the ^{29}Si–NMR spectra of experimental Si_3N_4 containing materials. The authors assigned it presumably to 'non-stoichiometric' silicon oxynitride phases.[8] Until recently, the composition and the structure of α-Si_3N_4 has been the subject of controversy.[11–16,18–20] Particularly, Wild *et al.* proposed in agreement with their structural determination and supported by oxygen analyses, that this phase was actually a silicon oxynitride phase where some nitrogen atoms are substituted by oxygen atoms and some nitrogen and silicon sites are vacant.[12] Jack suggested that the α-Si_3N_4 structure might be stabilized by the occurrence of Si^{3+} intersticials, the valence being compensated by oxygen atoms.[13] The former assumption was also proposed by Colquhoun *et al.* and accepted by Hendry, from thermodynamic considerations, to explain that the α-Si_3N_4 phase is experimentally more stable at higher oxygen partial pressures or at lower temperature.[15,16] Hence, the α-Si_3N_4 phase can be represented on thermochemical diagrams as an intermediate material of composition $SiN_{1·32}O_{0·03}$ ($\approx$ 2 at% of oxygen), between the β-Si_3N_4 (oxygen free) and Si_2N_2O. Conversely, some authors recently proved that although oxygen atoms might substitute nitrogen in α-Si_3N_4, there is no structural requirement for its presence.[19,20] For instance, an oxygen concentration as low as 0·05 wt% was measured in an α-Si_3N_4 single crystal.[20]

From the above discussion, it is suggested that the −56·4 ppm peak observed on the spectrum of the type C fibre may originate from the presence of $Si–N_3O$ tetrahedrons embedded in the α-Si_3N_4 structure of the fibre. The difference of magnitude of the chemical shift of this peak and those for the $Si–N_4$ sites in α-Si_3N_4 and the $Si–N_3O$ sites in Si_2N_2O, could be explained by differences in the chemical coordination and the tetrahedral geometry. A quantitative analysis of the ^{29}Si–NMR spectrum of the type C fibres accounts for a peak area ratio of the −56·4 ppm peak of 6 (±1·5)%. If one assumes that only $Si–N_3O$ sites are present in the structure of the fibre (the occurrence of an oxygen-richer silicon environment being improbable), the proportion of the $Si–N_3O$ sites calculated from an oxygen concentration of 1 to 2 at% would range from 4·5 to 8·8%, which is consistent with the value of the experimental peak area ratio. As a comparison, if the fibre was a mixture of pure Si_3N_4 and SiO_2, the proportion of $Si–O_4$ sites would have been only 1·1 to 2·4%.

The peak area ratio of the two α-Si_3N_4 resonance lines significantly differ from 50/50% (respectively, 52/42% for the −46·6/−48·8 ppm lines) for the type C fibre. This feature, in this case, cannot be attributed to the overlapping of an eventual β-Si_3N_4 resonance line (at −48·7 ppm) but rather tends to show that the silicon sites have not equivalent occupancy in the α-Si_3N_4 structure of the fibre. This phenomenon may also be related to the occurrence of specific $Si–N_3O$ sites in the structure of the fibre.

4.2 The type A fibres

The amorphous structure of the type A fibres is well established by both the XRD and NMR analyses. The absence of diffraction peaks on the XRD pattern denotes the extremely low crystalline order, which might not exceed 1 nm and the absence of narrow well defined peak on the NMR spectrum is indicative of a large spread in chemical bond length and/or angle. When compared to the reference crystalline samples (α-Si_3N_4, Si_2N_2O and α-Quartz), the extremely large band observed on the NMR spectrum of the type A fibres (ranging from −85 to −35 ppm) indicates a gradual change in local field resulting from the substitution of nitrogen atom(s) from the $Si–N_4$ tetrahedral environment by oxygen atom(s), forming mixed $Si–N_{4-n}O_n$ environments (with $n = 0, 1, \ldots, 4$) (Fig. 4).[7] The contribution of an SiO_2 layer on the NMR spectrum has been dismissed by XPS surface analyses. The oxygen is therefore considered to be homogeneously distributed through the fibre. No SiO_2 phase was detected by NMR since no resonance line at about −110 ppm was observed in the spectrum.[9,10] Furthermore, the large peak observed for the type A fibres cannot be associated to pure 'amorphous silicon nitride'. Funayama *et al.* investigated an amorphous Si_3N_4 fibre[21] and Carduner *et al.* studied an amorphous Si_3N_4 powder[8] by ^{29}Si–NMR analysis. The spectra obtained for these materials both showed a large peak of respective peak maxima of −46 and −46·4 ppm

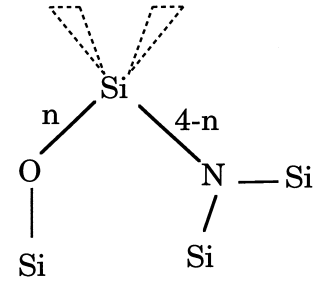


Fig. 4. Schematic description of the tetrahedral environment of silicon atoms $Si–N_{4-n}O_n$ ($n = 0, 1, \ldots, 4$), in Si–N–O ceramics.

and FWHHs of 15 and 27 ppm with a clearly symmetric line shape for the amorphous Si_3N_4 fibres.[21] The greater line width of the amorphous Si_3N_4 materials was in these cases only related to the heterogeneity in the Si local field, due to a spread in the distribution of bond length and angles, rather than a change in the chemical environment of Si, as suggested by the chemical shifts close to those for crystalline Si_3N_4 and the symmetric line shape. The above discussion has shown that the type A fibres are made of a single amorphous silicon oxynitride phase where the silicon atoms have mixed $Si–N_{4-n}O_n$ tetrahedral environments ($n = 0$, 1, ..., 4) (Fig. 4). If $Si–N_{4-nx}O_{n_x}$ ($0 < n_x < 4$) is the average tetrahedral environment of silicon atoms in the oxynitride phase, the chemical atomic composition of this phase can be written (straightforward from Fig. 4) $Si–N_{(4-n_x)}/3O_{n_x}/2$ or, if $x = n_x/4$ (with $0 < x < 1$), $Si–N_{4(1-x)/3}O_{2x}$.[5] In the case of the type A fibres (12–13 at% of oxygen), $x = 0{\cdot}1458$–$0{\cdot}1586$ (Table 3). The chemical shift and the shape of the NMR peak is therefore directly related to the relative intensities of the different NMR $Si–N_{4-n}O_n$ components and as a consequence, to the fraction of different tetrahedral sites in the material. The characteristic shifts of the resonance lines corresponding to all the different $Si–N_{-n}O_n$ sites cannot be precisely defined because of the lack of reference crystalline materials belonging to the Si–O–N system and containing $Si–N_2O_2$ or $Si–NO_3$ tetrahedral sites. The only reference sites reported for Si–N–O ceramics are $Si–N_4$, $Si–N_3O$ and $Si–O_4$, respectively involved in Si_3N_4, Si_2N_2O and SiO_2. The experimental values of the shifts corresponding to the latter sites as well as the shouldering visible on the lower shift side (−85 to −50 ppm) of the experimental resonance line however suggest that the magnitude of the shift of the different sites decreases approximately linearly—or at least continuously—with the number of oxygen atom(s) substituting nitrogen atom(s) in the Si environment. This assumption is confirmed by a MAS–NMR study of different Y–Si–O–N crystalline phases, involving the whole range of tetrahedral $Si–N_{4-n}O_n$ sites ($n = 0$, 1, ..., 4).[7]

An obvious possible structure of the silicon oxynitride phase is a random tetrahedral distribution of N and O atoms around the Si atoms of the material. The proportion of the five different $Si–N_{4-n}O_n$ ($n = 0$, 1, ..., 4) sites is in this case directly related to the oxygen (or nitrogen) concentration in the $SiN_{4(1-x)/3}O_{2x}$ material or, more precisely, to the ratio of Si–O bonds with respect to the total number of Si–O and Si–N bonds in the material, i.e. x (Fig. 4). The fraction of the different $Si–N_{4-n}O_n$ ($n = 0$, 1, ..., 4) tetrahedral sites is therefore:

$$P_n = C_n^4 \cdot X^n \cdot (1 - x)^{(4-n)} \qquad (1)$$

The values of P_n calculated for the type A fibres are shown in Table 3 and the distribution of the different $Si–N_{4-n}O_n$ ($n = 0$, 1, ..., 4) sites is compared to the experimental NMR peak in Fig. 5. There is a remarkable similarity between the calculated distribution of the different sites and the shape of the NMR peak. This semi-quantitative analysis confirms the assumption of a statistical distribution of N and O atoms around the Si atoms. A quantitative analysis was not attempted because of the lack of spectral parameters for the $Si–N_2O_2$ and $Si–NO_3$ bands and the complex shape of the NMR bands of pure amorphous compounds (neither Gaussian nor Lorentzian).[8]

Table 3. Distribution of the different tetrahedral sites in the type A fibres

O (at%)	x	P_0	P_1	P_2	P_3	P_4
12/ 13	0·1458/ 0·1586	0·5324/ 0·5012	0·3635/ 0·3779	0·0931/ 0·1069	0·0106/ 0·0134	0·0005/ 0·0006

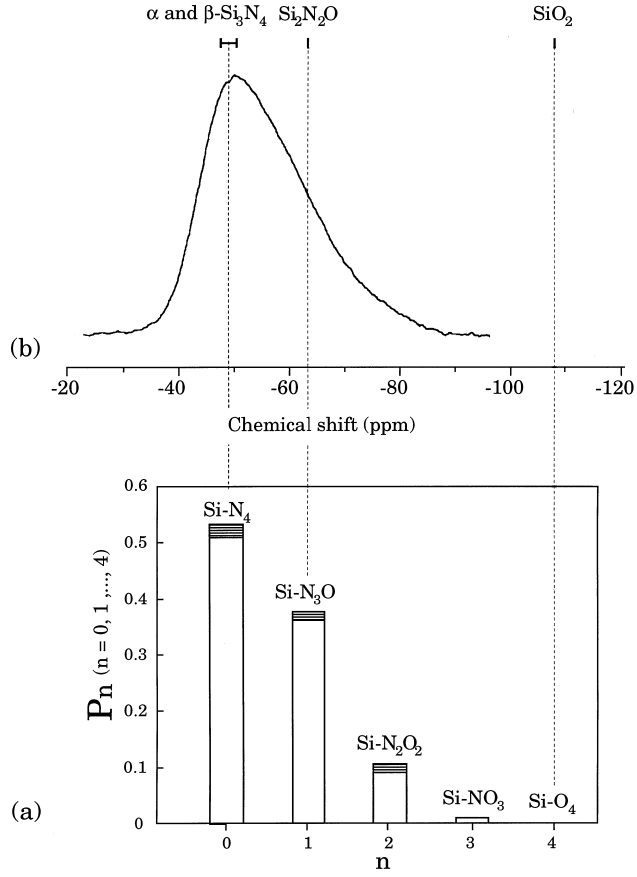


Fig. 5. Statistical distribution of the different $Si–N_{4-n}O_n$ ($n = 0$, 1, ..., 4) tetrahedral sites in (a) the silicon oxycarbide $Si–N_{4(1-x)/3}O_{2x}$ ($x = 0{\cdot}1458$–$0{\cdot}1586$) compared to (b) the experimental silicon-29 MAS–NMR spectrum of the amorphous silicon oxycarbide fibre.

5 Conclusion

The ^{29}Si–MAS–NMR technique was used in combination with elemental and XRD analyses to determine the composition and the structure of crystalline and amorphous Si–N–O fibres. The crystalline fibres (type C) were found to consist of mainly α-Si_3N_4 (98 wt%) and traces of β-Si_3N_4. The presence of oxygen was detected and suggested to be distributed within the α-Si_3N_4 structure as a silicon oxynitride phase, as already proposed in the literature. The anomalous silicon tetrahedral site where oxygen atoms substitute nitrogen atoms (presumably Si–N_3O sites) would give rise to an original NMR peak with a chemical shift of −56·4 ppm.

The amorphous fibres (type A) consist of an amorphous silicon oxynitride phase of homogenous composition Si–$N_{4(1-x)/3}O_{2x}$ (with $x = 0{\cdot}14$–$0{\cdot}16$ or 12–13 at% of oxygen). The silicon atoms in the material are surrounded by a mixed tetrahedral environment Si–$N_{4-n}O_n$ ($n = 0, 1, \ldots, 4$) consisting of O and N atoms statistically distributed. Nitrogen and oxygen atoms are, respectively, bonded to 3 and 2 silicon atoms. The five different tetrahedral sites give rise to five overlapping peaks of decreasing chemical shifts (from −110 to −48 ppm). The respective intensities of the different Si–$N_{4-n}O_n$ peaks and therefore, the global shape of the experimental NMR peak are related to the fraction of the Si–$N_{4-n}O_n$ sites and, as a consequence, to the oxygen concentration.

Acknowledgements

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