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NMR CHARACTERIZATION OF SILICON CARBIDES AND CARBONITRIDES. A METHOD FOR QUANTIFYING THE SILICON SITES AND THE FREE CARBON PHASE.

GERARDIN C., HENRY M. and TAULELLE F.
Laboratoire de chimie de la Matière Condensée, University P. et M. Curie, T54-55
4 Place Jussieu, 75252 Paris Cedex 05, FRANCE

ABSTRACT

With ceramics prepared from organic precursors, polymers are often formed by thermolysis, and the ceramics are obtained by pyrolysis of the polymer. This paper will cover the NMR methods used to characterize the polymerization as well as the pyrolysis of such polymers. The reticulation rate of such materials is measured on the silicon atoms and on the carbon atoms, leading to a silicon reticulation state and a carbon reticulation state. For the ceramics, the quantification of the SiC_xH_{4-x} or SiC_xN_{4-x} sites is performed using a priori chemical shift calculation. A measure of the H/C of the free carbon phase at the different temperatures of pyrolysis is presented. This measure uses a absolute determination of hydrogen content in ceramics, more accurate than a classical chemical analysis of hydrogen. The evolution of the reticulation, of the free carbon amount and of the H/C ratio in the free carbon phase will be followed with the temperature.

INTRODUCTION

Since the discovery of the Nicalon fiber new routes to silicon carbides have been constantly developed[1,2,3]. The goals are to reach a high molecular weight with a high ceramization yield combined in a high purity material. A starting material called PPCS with a linear formula $-(-SiH_2-C_2H_4-)_n-$ has been used to form a SiC ceramics[4]. The polymerization process has been a catalytic hydrosilylation[5]. This route leads to a ceramic precursor well defined, less complex than the Yajima's precursor PCS. Another family of compounds named PVSZ of general formula $-(-SiHVinyl-NH-)_n-$ lead to SiCN ceramics.
The goal of this contribution is not to describe the details of the materials condensation polymerization and ceramization but to show how NMR can be used to measure the parameters quantifying at each stage the evolution of the material.

CHEMICAL SHIFT IN AMORPHOUS PHASES

It has been shown that the screening constant of silicon can be calculated as follows[6]:

$$\sigma = \sigma_{dia} + \sigma_{para} = \sigma_{dia} - \frac{e^2\hbar^2 <r^{-3}>_p P_u}{3m_e c^2 \Delta E} \qquad (1)$$

Using the SDPCM (structure dependant partial charge model) [6] leads to a simplified expression of the chemical shift.

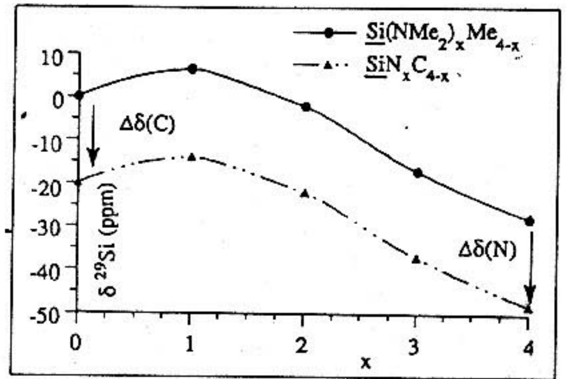

Figure 1: Chemical shift transposition from molecular to amorphous state in the SiN_xC_{4-x} system.

$$\delta = A - \frac{B(1+fq)^3 P_u}{C+Dq} \quad (2)$$

With A = 701 ppm, B = -1605 ppm, f = 0.873, C = 1.76eV and D = 9.25eV.

In the case of silicon (with the usual conventions) chemical shift noted as δ and screening constant noted σ have the same numerical values. In order to predict the chemical shift of a molecular or a structure compound, a knowledge of the positions of atoms in the structure or the distances and bond angles in a molecular entities is sufficient. However, one cannot estimate such a chemical shift in an amorphous material by such an approach. Furthermore, the chemical shift measured by NMR will always be the center of gravity of a distribution of chemical shifts related to sites in slightly different conformations.

Chemical shift estimation in amorphous material is therefore performed as follows, presented below for the SiN_xC_{4-x} system. First, the first sphere of coordination in which one is interested is taken on a family of molecular compounds. Here the family $Si(NMe2)_x(Me)_{4-x}$ has been considered.The chemical shift of these species can be calculated and measured. Both set of values are in excellent agreement. Then the series of solid samples can be measured, this is the case of SiC and Si_3N_4. In the case of amorphous SiC an approximate shift of -20 ppm is observed relative to liquid TMS. In the case of a first sphere of SiN_4 type in Si_3N_4, there is also a shift of -20 ppm compared to $Si(NMe)_4$. The chemical shift estimation for the three solid "unknown" mixed first spheres proceeds by translation of the complete series of molecular compounds chemical shifts by -20 ppm. Actually the estimation procedure is governed by the actual expression of the chemical shift.

$$\delta_n = 701 - \frac{1065\,(\,1 + 0.873\,q_n)^3\,P_u}{\Delta E_n}$$

For the mixed spheres SiN_xC_{4-x} the different terms can be treated as follows:

SiC4	SiC3N	SiC2N2	SiCN3	SiN4
-20 ppm	-14 ppm	-22 ppm	-37 ppm	-48 ppm
SiC4	SiC3O	SiC2O2	SiCO3	SiO4
-20 ppm	-10 ppm	-44 ppm	-73 ppm	-109 ppm
SiN4	SiN3O	SiN2O2	SiNO3	SiO4
-47 ppm	-58 ppm	-74 ppm	-90 ppm	-109 ppm
Si(CH2)4	SiHC3	SiH2C2	SiH3C	SiH4
20 ppm	6 ppm	-20 ppm	-51 ppm	-90 ppm

Table I: selected characteristic positions of mixed first spheres occuring in silicocarbides, silicocarbonitrides and silicocarboxides amorphous materials.

$\Delta E_n = (n\Delta E_4 + (4-n)\Delta E_0)/4$, the charges are estimated by $q_n = (nq_4 + (4-n)q_0)/4$ and the population unbalance is given by $P_u=1 - q_n^2/16$ [6].

This relation of the three parameters governing the chemical shift allows for a generalization of the chemical shift estimation starting with a knowledge of the molecular species and an "educated" transposition of those shifts to the solid state. The accuracy of the positions thus obtained is in the order of 2 to 5 ppm. This is lose enough to localize the center of gravity of a ditribution of sites in amorphous materials. This "assignment" provides a good way to attribute a peak to its correct first sphere. The final positioning is done on the experimental spectrum itself.

LOCAL SITE ENVIRONNEMENT OF SILICON

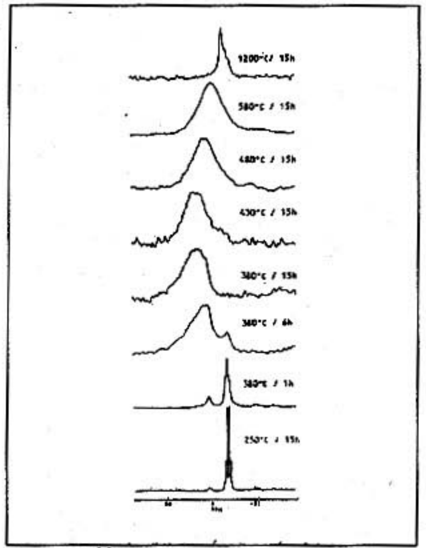

Figure 2: ^{29} Si MAS NMR of PPCS.

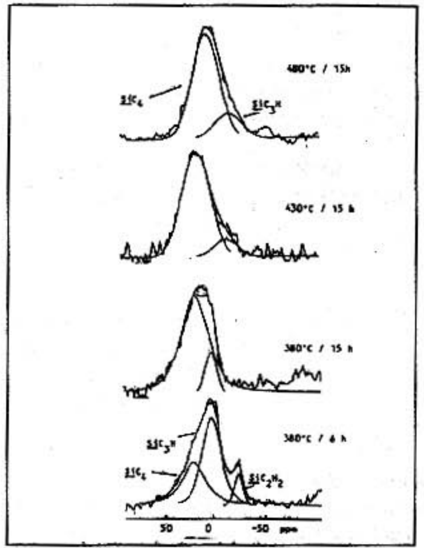

Figure 3: ^{29}Si MAS NMR decomposition.

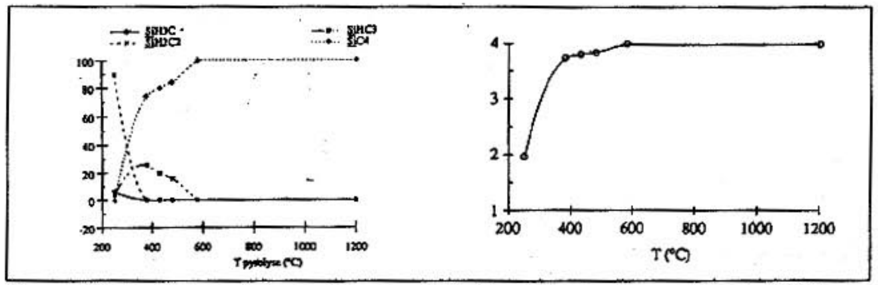

Figure 4: a) distribution of sites environnement; b) silicon functionality evolution in PCCS.

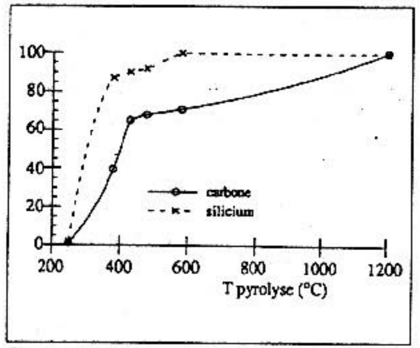

Figure 5: reticulation rate of PPCS;

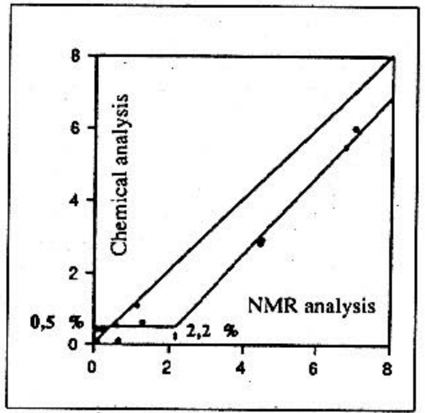

Figure 6: ${}^{1}H$ NMR and chemical analysis.

In the case of the PCCS (polycarbocarbosilane) of general formula -SiH2-C2H4-Si- the ${}^{29}Si$ NMR spectra in MAS conditions have been acquired for different temperatures treatments. In Figure 2 the ensemble of the spectra is presented. Figure 3 presents a selection of spectra, with their decomposition. This decomposition is done with positions fixed at their calculated values by the above procedure. Only the intensities and widths are fitted. The proportion of sites are therefore plotted as a function of temperature in Figure 4a, and the functionality "n" of silicon deduced figure 4b. The reticulation rate is calculated as n/4. By an analogous procedure the reticulation rate of the carbon has been measured and is given in figure 5.

HYDROGEN CONTENT MEASURE

While the ceramic is being formed, the C-H and the Si-H bonds are progressively replaced by C-Si and Si-C bonds. The amount of hydrogen in the sample is related to the reticulation of carbon and silicon. Usually hydrogen measurent is done through a chemical analysis of the sample. At low amounts of hydrogen, the chemical analysis is not reliable. A NMR measure of the areas of the ${}^{1}H$ peaks has been done on a series of PVSZ compounds, and the NMR results are plotted versus the chemical analysis ones in Figure 6. Under 2% in weight the chemical analysis gives erratic results. Above 2% they contain a systematic error, underestimating the results by 2.2%. For the PVSZ series of compounds the amount of hydrogen has been plotted on figure 7 as a function of the temperature. In the chemical analysis that will be used later on, the hydrogen elemental analysis has been systematically replaced by the NMR ${}^{1}H$ analysis.

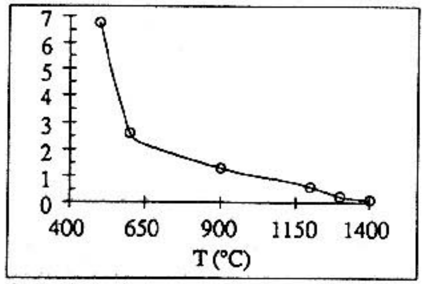

Figure 7: hydrogen content measured by NMR.

FREE CARBON PHASE MEASURE

As the results obtained in ${}^{29}Si$ MAS NMR allow measurement of the environment of the silicon, if the material is single phased, the analysis of the distribution sites in ${}^{29}Si$ is equivalent to performing a chemical analysis. A plot of this NMR elemental analysis versus chemical analysis appears in figure 8a for the PVSZ compounds. It is obvious that a large discrepancy between the two sets of values exists. This discrepancy is attributed to the fact that not all the atoms in the phase are connected to the silicon network. The material is not single phased, shown by electronic microscopy, it contains a "free carbon" phase. The relations between the chemical analysis and ${}^{29}Si$ NMR analysis are:

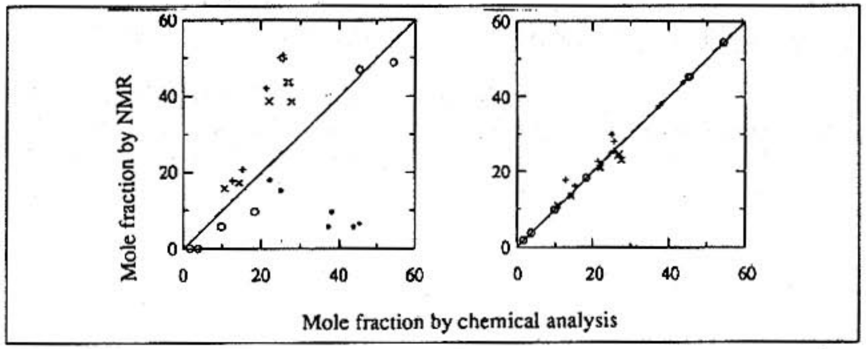

Figure 8: a) on left correlation NMR chemical shift without free carbon phase; b) on right with free carbon.

$$(3)\qquad 1 = x_C + x_H + x_{Si} + x_N \qquad {}^{29}\mathrm{Si\ NMR}$$

$$(4)\qquad 1 = X_C^{Si} + X_C^{free} + X_H^{Si} + X_H^{free} + X_{Si} + X_N \qquad \mathrm{Chemical\ analyis}$$

Renormalization of equation (3) leads to:

$$(5)\qquad 1 + x_C^{free} + x_H^{free} = x_C + x_C^{free} + x_H + x_H^{free} + x_{Si} + x_N$$

and combining (4) and (5) gives:

$$\begin{aligned}
X_C &= (x_C + x_C^{free}) / (1 + x_H^{free} + x_C^{free})\\
X_H &= (x_H + x_H^{free}) / (1 + x_H^{free} + x_C^{free})\\
X_{Si} &= x_{Si} / (1 + x_H^{free} + x_C^{free})\\
X_N &= x_N / (1 + x_H^{free} + x_C^{free})
\end{aligned}$$

with X_i are the molar fraction measured by chemical analysis and x_i the molar fraction measured by NMR. x_H^{free} and x_C^{free} are the fractions of hydrogen and carbon not measured by ${}^{29}Si$ NMR. The comparison of the two sets of results allows therefore for a complete determination of x_H^{free} and x_C^{free}. Both sets are now in agreement as plotted in Figure 8b. The amount of free carbon has been plotted in Figure 9 and the ratio H/C of the free carbon

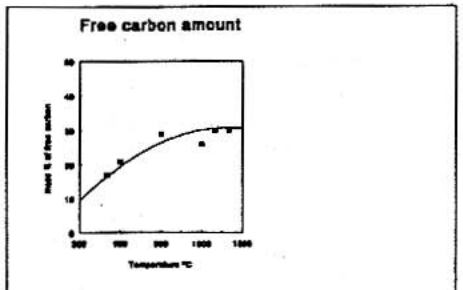

Figure 9: free carbon amount in PVSZ.

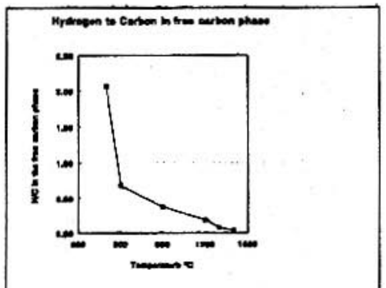

Figure 10: H/C ratio in the free carbon phase of PVSZ.

has been plotted in Figure 10. The H/C ratio evolution confirms previous work[7] on the formation of the free carbon phase, involving coronene formation. The coronene H/C ratio is 0.5. As the material has a starting H/C ratio of 2, the evolution through coronene and condensation of these basic structural units by sides to form the free carbon phase, is followed quantitatively with the present measurements.

CONCLUSION

Though the details of the mecanisms of the material transformation have not been treated in this paper, due to space limitations, it has been shown that most of the quantitative parameters describing the evolution of a series of polymeric, amorphous or crystalline materials can be identified through NMR combined with chemical analysis.The concepts used to describe the evolution through the amorphous state, up to the crystalline state, follow from polymer science.

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HIGH TEMPERATURE STABILITY OF OXYCARBIDE GLASSES

HANXI ZHANG AND CARLO G. PANTANO
Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pa 16802

ABSTRACT

The stability of silicon oxycarbide glasses has been studied at temperatures up to 1500°C. The silicon oxycarbide glasses were synthesized using a sol/gel process. The pyrolysis treatment in argon influenced the structure and composition of the synthesized glasses, and in turn, their high temperature stability in oxidizing atmosphere. The oxycarbide glasses pyrolyzed at $\geq$ 1000°C had lower hydrogen concentration and a more polymerized network structure, and thereby were more resistant to oxidation and crystallization at higher temperatures.

I. INTRODUCTION

The thermochemical and thermomechanical stability of glasses has always been a critical issue in their high temperature applications. Ordinarily, oxide glasses crystallize and soften at elevated temperatures. There has been great interest in enhancing the stability of the glasses by incorporating carbon into glass structures[1-2]. The sol/gel process has made it practical to synthesize these glasses[3-5]. Carbon offers the possibility of 4 coordinate bonds to replace the oxygen anion which is only 2 coordinate, and this is expected to strengthen the molecular structure of the glasses. Chi[2], Zhang and Pantano[4], and Runland[5] have independently reported that there was limited crystallization of SiO_2 from the oxycarbide glasses. But these oxycarbide glasses were processed and evaluated in very different ways. Thus, the goal of this study was to systematically examine the relationships between processing and high temperature stability. The gels were synthesized using an established procedure and they were pyrolyzed to the glassy state in argon over the temperature range 800°C to 1400°C. Solid state Magic Angle Spinning ^{29}Si Nuclear Magnetic Resonance (MAS ^{29}Si NMR), ^{13}C NMR and chemical analysis were used to characterize these glasses. The decomposition and oxidation resistance was examined by thermogravimetric analysis (TGA). The role of glass structure and composition in the thermochemical stability will be discussed.