Journal of the European Ceramic Society **8** (1991) 215–219

Nanometric Si/C/N Composite Powders: Laser Synthesis and IR Characterization

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(Received 2 January 1991; revised version received 23 February 1991; accepted 11 March 1991)

Abstract

Synthesis of nanometric Si/C/N composite powders from pyrolysis of binary and ternary SiH_4–CH_3NH_2–NH_3 gaseous mixtures, with a continuous-wave CO_2 laser, is reported. The composition of powders obtained under particular conditions is very similar to those which lead to densified materials presenting superplasticity phenomenon. The bulk characterization of the ceramic by infrared spectroscopy suggests that it is not a simple juxtaposition of SiC and Si_3N_4. The infrared surface spectrum reveals the presence of interatomic bonds between Si, C and N on the surface.

Durch SiH_4–CH_3NH_2–NH_3 Gemische, die mit einem Dauerlicht-CO_2 Laser pyrolysiert werden, werden nanometrische komposite Si/C/N Pulver hergestellt. Die Pulver haben eine Zusammensetzung, die jener von gesinterten Festkörpern, die das Phänomen der Superplastizität aufweisen, entspricht. Die infrarotspektroskopische Untersuchung des Körperinneren zeigt, daß dieses Material nicht nur eine einfache Mischung von SiC und Si_3N_4 ist. Das IR Spektrum der Oberfläche bestätigt das Vorhandensein von interatomischen Bindungen zwischen Si, C und N in diesen Bereich.

On présente la synthèse de poudres nanométriques composites Si/C/N par pyrolyse de mélanges gazeux binaires et ternaires (SiH_4–CH_3NH_2–NH_3) au moyen d'un laser CO_2 continu. Des poudres obtenues dans des conditions spécifiques ont une composition proche de celles qui ont conduit à des objets densifiés présentant le phénomène de superplasticité. La caractérisation par spectrométrie infra-rouge du coeur du matériau indique qu'il n'est pas une simple juxtaposition de SiC et de Si_3N_4. Le spectre de surface met en évidence la présence en surface de liaisons interatomiques entre Si, C et N.

1 Introduction

Si_3N_4 and SiC are promising materials with high-temperature engineering applications. Sintered materials obtained from Si_3N_4–SiC composite powders have been shown to present better strength properties at high temperatures than Si_3N_4.[1,2] Recently superplasticity properties were found for the hot-pressed crystal composite Si_3N_4–SiC.[3,4] The use of finer Si_3N_4–SiC or Si/C/N composite particles, involving a more uniform dispersion of the phases, would greatly improve their properties. Such useful nanometric powders can easily be obtained from vapour phase reaction, which is induced by CO_2 laser radiation in the synthesis of Si/C/N composite powders.[5,6] This study deals with the laser synthesis of two Si/C/N composites with different C/N ratios (0·6 and 0·2) and an infrared characterization. The samples were prepared from different gas reactant mixtures (SiH_4, CH_3NH_2, NH_3) and both bulk composition and surface structure are obtained from the absorption infrared spectra.

Journal of the European Ceramic Society 0955-2219/91/$3.50

2 Experimental

The experimental device used in the synthesis has been described previously.[7,8] The unfocused beam (diameter = 12 mm) of a continuous-wave CO_2 laser enters the reaction cell (Fig. 1) through a KCl window and crosses the gaseous flow of the reactants injected through an inlet capillary (inner diameter = 2 mm). A resonance effect between the light emitted by the CO_2 laser and an infrared band of one of the reactant gas causes the reaction to occur.[8] This laser-driven reaction brings about high temperature and bright flame. An argon flow (2 litres/min) prevents powder deposition on the windows, and guides the products in the collection chamber. The powders are stored in a glove-box to avoid contamination by air or water vapour. Specific surface area (S_{BET}) is determined from BET measurements. The C, N and O contents are obtained by chemical analysis; the Si content is calculated as that remaining. The chemical composition is obtained by assuming a total conversion of C, N and O to SiC, Si_3N_4 and SiO_2, respectively, and the difference to 100% leads to the free Si content. In some cases, as shown, free carbon can be present. The particle morphology is determined by transmission electron spectroscopy and the crystalline phase by X-ray diffraction. By varying either the total flow rate and its composition or the laser power it was easy to change the size and the crystallinity of the powders.

The infrared spectra were recorded using a Fourier transform infrared spectrometer (Nicolet 5DX) in the 4000–400 cm^{-1} range. For studying the bulk the Si/C/N powder was pressed in a KBr pellet (0·3 wt%). For the surface investigation the powder was pressed in thin pellets (diameter = 20 mm, wt = 150 mg) on a grid (from Gantois, Saint-Dié, France) and then placed in a greaseless cell connected to a vacuum line specially designed for running in-situ experiments. The sample was heated under vacuum or deuterium gas at controlled pressure and cooled to room temperature. This experimental procedure has already been applied to pure Si_3N_4[9] and pure SiC[10] high surface area samples. The quality of the spectra was rather poor, more particularly in the 4000–3000 cm^{-1} range. This was partly due to the presence of free carbon generating an important dispersion effect. In addition, the weakness of the signal made the evolution of certain bands difficult to detect; they could only be seen on difference spectra.

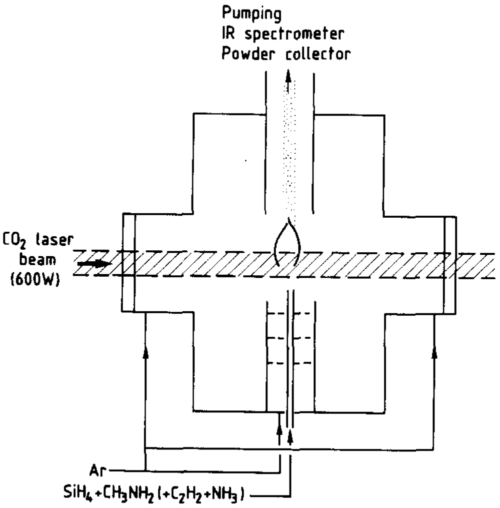

Fig. 1. Schematic irradiation cell.

3 Results and Discussion

3.1 Laser synthesis

Several mixtures were investigated. Firstly, composites were synthesized from a binary mixture $SiH_4 + CH_3NH_2$, in which the flow rate of reactants were 220 and 320 cm^3/min, respectively (1/1·5 composition). The cell pressure was always kept constant at 10^5 Pa (1 atm). The carbon and nitrogen contents could be modified ($0·6 < C/N < 0·97$) by changing the other experimental parameters. A ternary mixture was then studied: $SiH_4 + CH_3NH_2 + NH_3$. The composition of gas reactants was 1/0·25/0·9 with different total flow rates, typically 280, 70 and 250 cm^3/min, respectively. The presence of NH_3 is known to make the nitridation easier and so the nitrogen content was expected to increase. The C/N atomic ratio varied from 0·17 at the lowest reaction temperature to 0·23 at the highest one, although the initial C/N in the gaseous mixture stayed fixed at 0·22. The oxygen content remained low and varied from 0·6 to 1·5 wt%. Experiment duration varied between 20 and 45 min, and an amount of powder up to 28 g was collected. The laser synthesis results reported concern powders with a C/N atomic ratio near 0·2, for which the superplasticity phenomenon was observed after sintering. Figure 2 shows the variations of the brightness temperature of the reaction flame versus three values of the total flow rate (600, 770 and 940 cm^3/min) for three values of the laser power (400, 500 and 600 W). The variations of the specific surface area versus the same values of total flow rate and for the three laser powers are given in Fig. 3. The highest specific surface area (i.e. the smallest particle diameter) is obtained for the shortest residence time and the lowest power, as reported for SiC laser synthesis.[7] Neglecting Si and SiO_2 and assuming a

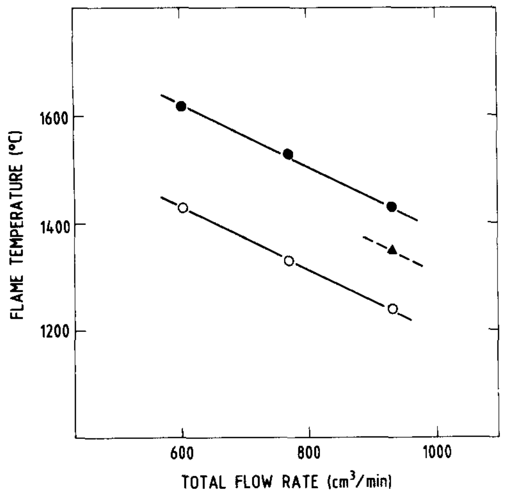

Fig. 2. Flame temperature of Si/C/N laser synthesis reactions. Laser power: ○, 400 W; △, 500 W; ●, 600 W.

mean density of 3·2, near the densities of SiC and Si_3N_4, the calculated particle size varies from 30 nm ($S_{BET} = 49\,m^2/g$) to 72 nm ($S_{BET} = 26\,m^2/g$). These values are confirmed by electron microscopy observation. The crystalline phases (free Si, β-SiC, α-Si_3N_4 or β-Si_3N_4) which are formed at high temperatures are identified by X-ray diffraction. At low temperatures amorphous powders are formed without any real identification of a SiC or Si_3N_4 phase.

3.2 Infrared characterization

For this study samples were synthesized from a $SiH_4 + CH_3NH_2$ mixture irradiated with 600-W laser power at 1180°C.[6] The C/N ratio was 0·66 with 10 wt% free silicon and $S_{BET} = 111\,m^2/g$.

3.2.1 Study of the bulk of the compound

The infrared spectrum of the bulk is shown in Fig. 4. It exhibits a band at 878 cm^{-1} (half-width equal to 240 cm^{-1}). The profile of this band is not the same as that of SiC or Si_3N_4 (Fig. 5). The wave-number of the maximum absorption is situated between those of stoichiometric Si_3N_4 (950 cm^{-1}) and SiC (840 cm^{-1}). The half-width of this band should suggest that the sample is not simply a physical mixture of the SiC and Si_3N_4 compounds. A weak band observed at 470 cm^{-1} is assigned, as in Si_3N_4,[11,12] to the Si–N–Si deformation mode.

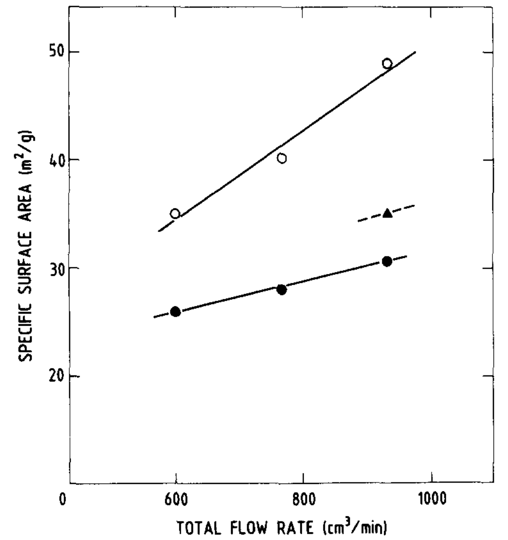

Fig. 3. Specific surface area of Si/C/N laser-synthesized powders. Laser power: ○, 400 W; △, 500 W; ●, 600 W.

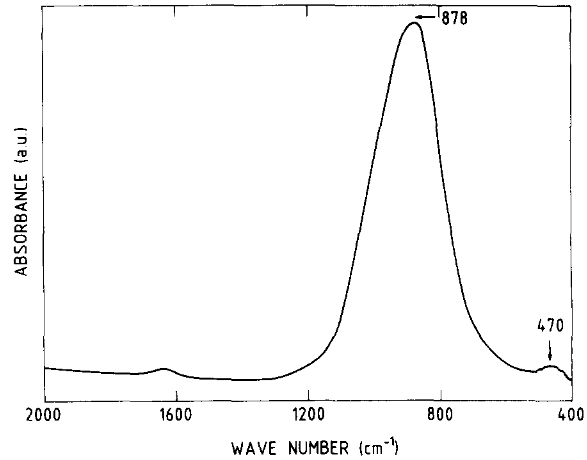

Fig. 4. FT-IR absorbance spectrum of the bulk of a Si/C/N sample (C/N = 0·66). KBr pellet: 1 mg/350 mg.

3.2.2 Study of the surface of the compound

The amount of sample needed to study the surface obscures the range below 1200 cm^{-1}, where the absorption of the bulk falls. Heating up to 500°C under vacuum (activation) cleans the surface of all the physisorbed and most of the chemisorbed species. The spectrum of the activated sample (Fig. 6, curve a) exhibits a sharp absorption at 3744 cm^{-1} and also broad and rather weak bands around 3350, 2290 and 2230 cm^{-1}. The sharp band is close to the

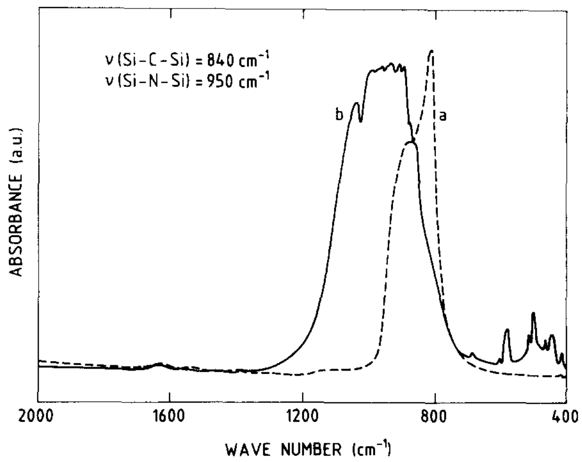

Fig. 5. FT-IR spectrum of laser-synthesized stoichiometric and crystallized powders: a, silicon carbide; b, silicon nitride.

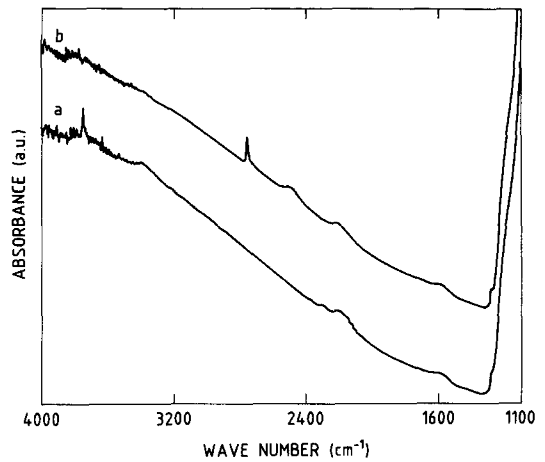

Fig. 6. FT-IR surface spectra of high surface area Si/C/N: a, after activation, i.e. clearing out, under vacuum and high temperature (500°C), all the physisorbed and most of the chemisorbed species; b, after deuteration of surface species (D_2 gas, 500°C, 15×10^3 Pa).

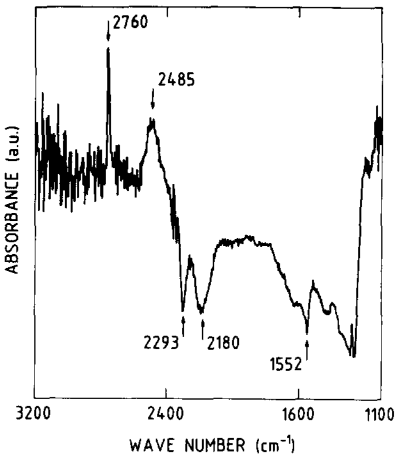

Fig. 7. Difference spectrum (from Fig. 6; b − a). Positive and negative bands respectively correspond to species appearing and disappearing during deuteration.

value observed in silica for the OH stretching vibration.[13]

After adding two subsequent doses of deuterium gas (15×10^3 Pa each) at 500°C, the 3744 cm^{-1} band no longer exists, but two new absorptions are observed at 2760 and 2485 cm^{-1}. The creation of the 2760 cm^{-1} band associated with the removal of the 3744 cm^{-1} band allows an unambiguous assignment of this latter frequency to the OH stretching vibration in silanol groups, all of them located on the surface. Similar groups have been observed on SiO_2, SiC, Si_3N_4 and Si_2N_2O surfaces.[9,10,13,14] By comparison with the study of Si_3N_4 the 2485 cm^{-1} band appearing after deuteration is assigned to the N–D stretching mode. The corresponding N–H vibration is expected at 3350 cm^{-1},[9] which was noted previously as a weak and broad feature partly masked by the noise. Lastly, the 2230 cm^{-1} weak band is still present in the spectrum of the deuterated sample. Thus it is not affected by the isotopic exchange and it may reasonably be assigned to an overtone or a combination of the bulk vibrations.

The difference spectrum (before and after deuteration) (Fig. 7) brings better evidence of the appearing and disappearing species (positive and negative bands, respectively). The negative band at 1552 cm^{-1} is assigned, in comparison to Si_3N_4,[9,15] to the scissoring vibration of the NH_2 group disappearing under deuteration, while the isotopically exchanged ND_2 group absorbs below 1200 cm^{-1} (i.e. the range where bulk absorption obscures the spectrum). The corresponding stretching modes which should be located at 3510 and 3450 cm^{-1} could not be detected by virtue of their weak intensity in a noisy region. In addition, two negative bands (2293 and 2180 cm^{-1}) fall in a range well known[16] to be related to the Si–H stretching mode whose absorption wave-number is very sensitive to the silicon environment. The 2180 cm^{-1} band was also observed in Si_3N_4[9,15] and assigned to the stretching vibration of a surface Si–H group in a nitrogen environment. Moreover, a drastic nitridation of SiC (naturally slightly oxidized on its surface) has yielded $HSiO_xN_y$ species absorbing at 2295 cm^{-1},[10–15] not very different from the 2285 cm^{-1} value observed with Si_3N_4 for the same species. Therefore the 2293 cm^{-1} band may reasonably be attributed to the $HSiO_xN_y$ species, whose environment should be similar to that in nitrided SiC.

4 Conclusion

The authors have shown the adaptability and the versatility of the CO_2 laser synthesis process for obtaining Si/C/N composite powders with variable characteristics (chemical composition, size, crystallinity, etc.). The infrared study of a Si/C/N composite powder definitely confirms, on the surface, the existence of nitrogen atoms bonded to silicon. The presence of surface carbon atoms appears less clearly; it is only revealed by the Si–H absorption band, observed at the same frequency as in nitrided silicon carbide. This can be correlated with the carbon deficiency in the compound (C/N = 0·66). These samples are still under investigation by other characterization methods, such as XPS, ESCA, EXAFS or ^{29}Si MAS-NMR.

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