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^{29}Si MAS NMR Study on Quantitative Analysis of the Amorphous Phase in a Si_3N_4 Powder

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NMR study has been used for measuring precise quantity of the amorphous phase in the Si_3N_4 powder. Care must be taken to allow the ^{29}Si nuclear spin system to fully relax between pulses in order to make the signals proportional to the number of nuclei in each phase. ^{29}Si MAS NMR spectrum was decomposed into the three spectra of α-, β-, and amorphous Si_3N_4 assuming pseudo-Voigt function. Moreover, the Rietveld analysis of the powder X-ray diffraction data was performed to measure quantity of crystalline phases as α/β ratio.

Key words: NMR, Silicon nitride, Amorphous, Quantitative analysis, Relaxation time

I. Introduction

Silicon nitride (Si_3N_4) has been investigated since the 1950s[1] because of its potential application in refractories, cutting tools, engine wear parts, and biomedical implants. Because the crystalline and amorphous phases of Si_3N_4 and impurities such as silicon oxynitrides and silicates have different thermal expansion and oxidation susceptibilities, this difference strongly affects sinterability and final ceramic mechanical properties. Some amorphous Si_3N_4 can aid densification of the final material.[2] In view of the effects of the crystalline and non-crystalline phases and impurities on sinterability and its final ceramic mechanical properties, it is of vital importance to have reliable methods for measuring the quantities of α-, β-, and amorphous Si_3N_4 as well as impurities in batches of Si_3N_4 powder before carrying out final product formation and sintering. The powder X-ray diffraction (XRD) technique[3] that has been used to study those materials usually provides poor information regarding the amorphous phase of Si_3N_4 and non-crystalline impurities. All amorphous species contribute to the background diffraction signal whose intensity is difficult to quantify. Thus, ^{29}Si Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) that is sensitive to local structures has been performed in this study together with XRD technique. ^{29}Si NMR spectroscopy is easily applied to the analysis of Si_3N_4. Since ^{29}Si has a spin of 1/2, there are no quadrupole couplings to broaden the NMR lines.[4] Low ^{29}Si natural abundance (4.70%) makes the average dipolar coupling smaller. Previously reported study[5] that has been quoted as standard literature citation on the quantitative analysis has large experimental errors due to mistaken estimation of pulse delay time, the low-resolution NMR spectra, and how to decompose spectra into the three peaks of α-, β-, and amorphous Si_3N_4. Most importantly, care must be taken to allow the ^{29}Si nuclear spin system to fully relax between pulses in order to make the signals proportional to the number of nuclei in each phase.

The purpose of the present study is to establish how to quantify amorphous Si_3N_4 precisely. ^{29}Si MAS NMR was performed to measure the quantity of amorphous Si_3N_4 in the commercial Si_3N_4 powder. Normally, a wait of five times the longest spin-lattice relaxation time, T_1, (α-Si_3N_4) is required between repetitions of the experiment when using 90° pulses. ^{29}Si MAS NMR spectrum was decomposed into the three spectra of α-, β-, and amorphous Si_3N_4 assuming pseudo-Voigt function. Moreover, the Rietveld analysis[6] of the powder XRD data was performed to measure quantity of crystalline phases as α/β ratio.

II. Experimental Procedure

1. Sample Preparation for Measuring Reference Spectra

It is important to use homogeneous standard samples for measuring reference spectra of pure α-, β-, and amorphous Si_3N_4 before quantifying amorphous Si_3N_4 in the commercial Si_3N_4 powder. Three standard samples of α-, β-, and amorphous Si_3N_4 were prepared using the imide decomposition method which is known to give high-quality Si_3N_4 pow-

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der.[7] $Si(NH)_2$ was prepared using the ammonolysis of $SiCl_4$. $Si(NH)_2$ was decomposed to amorphous Si_3N_4 by calcination at 800 °C. Crystallization of α-Si_3N_4 was achieved by heating the amorphous Si_3N_4 powder at 1500°C and 1750°C. β-Si_3N_4 was prepared by calcining the amorphous Si_3N_4 powder with the addition of Y_2O_3 (<0.1 wt%) at 1750 °C.

2. ^{29}Si Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy

The NMR analysis was performed on a Chemagnetics CMX-300 spectrometer, using 4 kHz magic angle spinning. The resonance frequency employed was 59.7 MHz for ^{29}Si. A standard Chemagnetics 7.5 mm "pencil' model probe was used with a ZrO_2 rotor. The magic angle was set prior to insertion of the sample by optimizing the response of the ^{79}Br signal of the spinning sidebands of KBr (Maciel's method).[8] Pulse length was calibrated prior to analysis using silicone rubber. A single pulse sequence has been used for measuring reference spectra of pure α-, β-, and amorphous Si_3N_4 and for quantifying the amorphous phase in the commercial Si_3N_4 powder. All free induction decays were subjected to standard Fourier transformation and phasing. The chemical shifts are referenced to silicone rubber whose resonance was checked by inserting it into a MAS rotor in the presence of a Si_3N_4 sample (−22.333(8) ppm, more than 2 kHz magic angle spinning).[9] Negative shift represents environments more heavily shielded. Pattern decomposition of the spectrum was performed assuming pseudo-Voigt functions.

3. X-ray Diffraction Measurement and Data Analysis

The commercial Si_3N_4 powder to quantify α-, β-, and amorphous Si_3N_4 was well mixed with a NIST Si powder (a=5.43094 Å) for angular calibration. The XRD profile of the mixed sample was collected at room temperature with a conventional X-ray powder diffractometer (MXP^{3VA}, MAC Science Co.; CuKα radiation; step-scan mode; step width = 0.02° in 2θ; fixed time=5 sec; 2θ range=18-150°). The structural refinement was performed using a Rietveld analysis program "RIETAN".[6] Rietveld method has high accuracy in the quantitative crystalline phase analysis of silicon nitride due to whole powder pattern fitting.[3] This method is also very effective for the complicated powder diffraction data due to assuming crystal structural data. The peak shape was assumed to be a modified pseudo-Voigt function with asymmetry. The background of each profile was approximated by a six-parameter polynomial in $2\theta^n$, where n was a value from 0 to 5. The refinement of α- and β-phases was undertaken in the structure models which were proposed by Kato[10] and Grün,[11] respectively. For the α-phase, space group was assumed to be $P3_1c$ (trigonal, Z=4). The refinement of the β-phase was undertaken in the $P6_3$ space group (hexagonal, Z=2). The preferred orientation parameters, positional parameters, isotropic atomic displacement parameters, and occupational factor were fixed in the refinement. The weight fraction of α-phase w_α was calculated using following equation.[12]

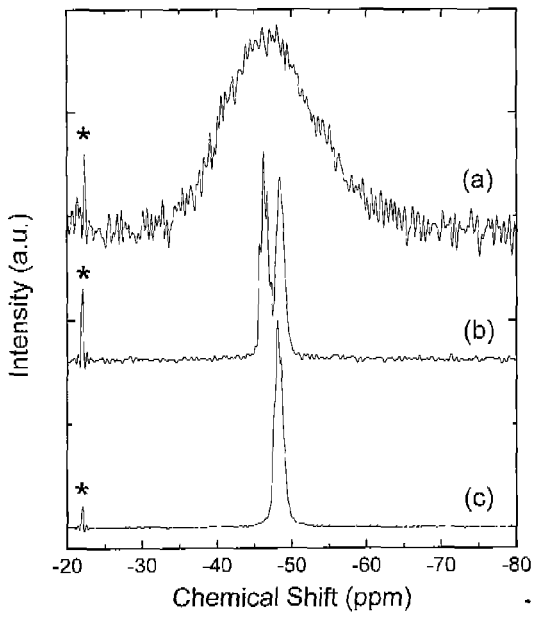

Fig. 1. ^{29}Si MAS NMR spectra of the three known phases of Si_3N_4. The sharp lines at −22.333(8) ppm (*) are from the silicone rubber internal reference: (a) amorphous Si_3N_4, (b) α-Si_3N_4, and (c) β-Si_3N_4.

$$w_\alpha = \frac{S_\alpha V_\alpha Z_\alpha}{S_\alpha V_\alpha Z_\alpha + S_\beta V_\beta Z_\beta} \quad (1)$$

where S_α, V_α, and Z_α are the scale factor, the unit-cell volume, and the number of formula units per unit cell of α-phase, respectively.

III. Results and Discussion

1. Reference Spectra of pure α-, β-, and Amorphous Si_3N_4

The NMR spectra of the three phases of Si_3N_4 are illustrated in Fig. 1. XRD has shown each of the crystalline samples to be at least 99±1 wt % of the major component as α/β or β/α ratios. No crystalline features were recorded in the XRD pattern of the amorphous Si_3N_4 sample. The spectra of the standard α-, β-, and amorphous Si_3N_4 sampls agree with those presented.[5] Two main peaks appear in the α-Si_3N_4 spectrum since this phase contains two unique silicon positions. β-Si_3N_4 has only one unique site and thus only one

Table 1. NMR Spectral Parameters of the Standard Si_3N_4 Samples Determined by Pseudo-Voigt Function Fitting

Phase	Peak maximum position (ppm)	FWHM (ppm)	Lorenzian ratio
α	−46.686(6)	1.23(2)	0.00(6)
	−48.812(7)	1.30(2)	0.39(6)
β	−48.605(3)	1.340(9)	0.25(2)
Amorphous	−47.09(3)	13.3(1)	1

main peak in its MAS spectrum. A thorough analysis of the NMR data reveals additional fine structure in the main peaks of the α- and β-Si_3N_4 spectra. This could be due to ^{29}Si-^{14}N residual quadrupole-perturbed dipolar coupling.[13-14] The shape of resonance peaks of the amorphous and crystalline phases corresponded to pseudo-Voigt function line shape. The peak maximum position, the full-width at half-maximum (FWHM), and the Lorenzian ratio from all three spectra are shown in Table 1. The greater line width of the amorphous phases is related to heterogeneity of local silicon electronic environments, which is a typical property of amorphous phases.

2. Measuring Quantity of α-, β-, and Amorphous Si_3N_4 in the Commercial Si_3N_4 Powder

The quantity of α-, β-, and amorphous Si_3N_4 in the commercial Si_3N_4 powder has been measured. ^{29}Si MAS NMR

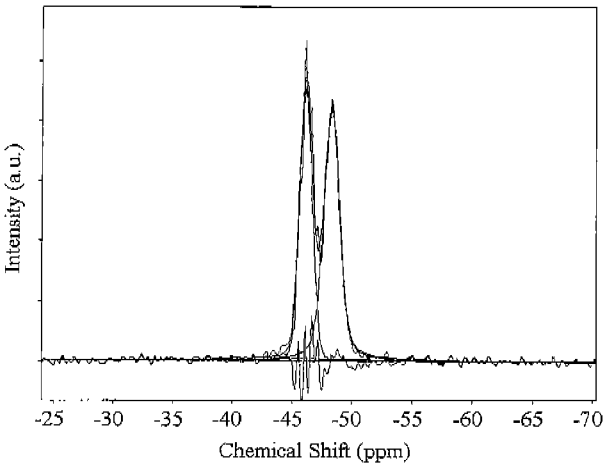

Fig. 2. ^{29}Si MAS NMR spectrum of the commercial Si_3N_4 powder. This spectrum was decomposed into the three spectra of α-, β-, and amorphous Si_3N_4 assuming pseudo-Voigt function.

that is sensitive to amorphous phases has been performed together with XRD technique. Most importantly, the differences in T_1 must be taken into account in the determination of the relative concentration of different phases of silicon nitride. Because ^{29}Si does not suffer from quadrupolar interactions, if care is taken to allow the ^{29}Si nuclear spin system to fully relax between pulses, peak areas in such spectra are directly proportional to the total number of Si atoms in each phase. A rather wide dispersion of T_1 values has been reported for the phases of Si_3N_4: 284±29 (–46.686 ppm), 260±23 (–48.812 ppm) min for α-phase, 36±4 min for β-phase, and 11±1 min for the amorphous phase.[15] In the previous study reported by Carduner *et al.*,[5] the pulse delay time has been estimated with large error; the use of 75° read pulses requires a wait of more than four times the longest T_1 when assuming following equation. If we use pulses having a flip angle θ, and apply them every T_r seconds, then the steady state magnetization M set up is given by

$$M = M_0\left[\frac{1-\exp(-T_r/T_1)}{1-\exp(-T_r/T_1)\cos\theta}\right] \quad (2)$$

where M_0 is the equilibrium magnetization.[16] Normally, a wait of five times the longest T_1 is required between repetitions of the experiment when using 90° pulses. In the present case, this would be about 1420 min, which has been taken in this study. ^{29}Si MAS NMR spectrum of the commercial Si_3N_4 powder was decomposed into the three peaks of α-, β-, and amorphous Si_3N_4 assuming pseudo-Voigt function as shown in Fig. 2. Here the NMR line shapes of individual Si_3N_4 phases are assumed to be the same as that of reference spectra; peak maximum positions and Lorenzian ratios of α-, β-, and amorphous phases and FWHM of the amorphous phase were fixed as those of reference spectra shown in Table 1 because it was difficult to decompose it due to almost near peak positions among spectra of α-, β-, and amorphous Si_3N_4. But nevertheless, it is fortunate that there is no need to consider the dependence of the spectrum

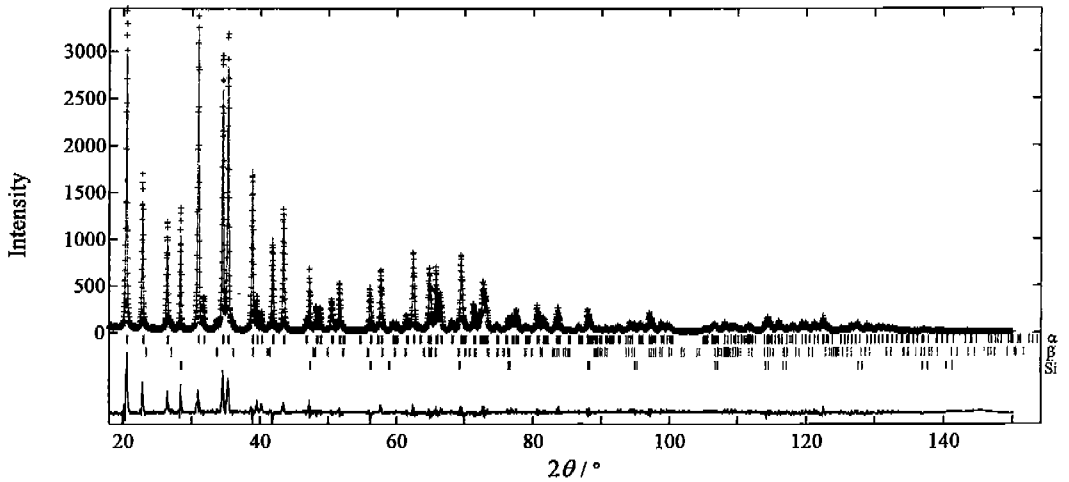

Fig. 3. (+) Observed and (–) calculated powder XRD pattern of the commercial Si_3N_4 powder. Vertical bars represent the positions of possible Bragg reflections. The differences between observed and calculated XRD intensity are shown beneath the figure in the same scale.

intensity on the frequency. The FWHM of the α-Si_3N_4 spectrum of the commercial sample was larger than that of the α-Si_3N_4 standard sample. The integral intensities of spectra were assumed to be directly proportional to the relative concentration of each phase. This assumption was safely made since care was taken to ensure complete T_1 relaxation. The result of the analysis shows there exists 8 wt% of amorphous Si_3N_4 in the commercial Si_3N_4 sample. Moreover, the Rietveld analysis of the powder X-ray diffraction data was performed to measure quantity of crystalline phases as α/β ratio. The refinement for the commercial sample was successfully performed in the structure models that were proposed by Kato[10] and Grün[11] (Fig. 3). The weight fraction of α-phase was calculated using scale factors refined by the Rietveld analysis[6]; w_α= 98.27(9) wt %.

IV. Conclusions

In this report we have proposed how to quantify amorphous Si_3N_4 precisely. Most importantly, the differences in T_1 must be taken into account in the determination of the relative concentration of different phases of silicon nitride. Normally, a wait of five times the longest T_1 is required between repetitions of the experiment when using 90° pulses to quantify amorphous Si_3N_4. ^{29}Si MAS NMR spectrum was decomposed into the three spectra of α-, β-, and amorphous Si_3N_4 assuming pseudo-Voigt function. Moreover, the Rietveld analysis[6] of the powder XRD data was performed to measure crystalline phases as α/β ratio. These techniques for their accurate identification and quantitation of amorphous phases at low concentration can provide an important tool for studies into the control of physical properties and microstructures for improved ceramic performance not easily studied by other techniques.

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