Quantitative analysis of SiC polytype distributions by the Rietveld method

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The quantitative determination of SiC polytype distributions is very difficult using traditional X-ray powder diffraction quantitative analysis methods, because the diffraction patterns of the various polytypes partially superimpose. The whole pattern fitting technique encapsulated in the Rietveld method is introduced to solve this problem. The detection limits for each polytype can be estimated based on their standard deviations. The results of both synthesized and experimental diffraction data show that the Rietveld method can give precise and accurate percentage compositions of the four most common SiC polytypes. This approach provides a practical tool to relate the preparation conditions to performance properties of SiC-based materials.

1. Introduction

Silicon carbide occurs in a number of different structural modifications known as polytypes, that have differing physical properties. The observed properties for dense silicon carbide samples strongly depends on the relative amounts of the various polytypes. It is therefore important to find an efficient way to quantitatively determine the SiC polytype distributions.

X-ray powder diffraction is a method that can be applied to determine the SiC polytype distributions. A considerable number of papers have been published in the literature that concern various aspects of the mesurement of relative contents of SiC polytypes. These papers have been reviewed by Frevel *et al.* [1] who note that these methods are based on the relation of several diffraction intensities with the percentage compositions of the polytypes. These results are strongly dependent on systematic errors introduced by the instrumental configuration and sample imperfections. In addition no corrections are applied to the factors that have significant influence on the diffraction intensities, such as preferred orientation and extinction. Furthermore, a considerable overlap of individual peaks of the X-ray powder diffraction patterns for the SiC polytypes occurs. This is because the polytypes are derived from the same parent structures but contain different stacking faults to each other. This situation makes it very difficult to obtain an accurate result for the distribution of the polytypes in a mixture.

In this work, the Rietveld refinement of X-ray powder diffraction data [2, 3] is applied to this problem. The principle is described and the technique is applied to synthesized and real SiC diffraction data. The results show that this is a highly effective approach to solving the problem.

2. The Rietveld method

For a diffractometer with Bragg–Brentano geometry and a diffracted beam monochromator, the intensity (I_{rj}) of a diffraction line r of a phase j in a sample can be written as:

$$I_{rj} = \left(\frac{I_0 \lambda^3}{32 \pi R_0} \frac{e^4}{m^2 c^4} \frac{V}{2} \right) \left(\frac{1}{V_{oj}^2} P_{rj} |F_{rj}|^2 \right.$$

$$\left. \times \frac{1 + \cos^2 2\theta_{rj} \cos^2 2\theta_\alpha}{\sin^2 \theta_{rj} \cos \theta_{rj}} e^{-2M_{ri}} \frac{1}{\rho_j} \right) D_{rj} \frac{X_j}{\mu} \quad (1)$$

where, λ is the wavelength of incident X-ray; m and e the mass and charge of electron; R_0 is the radius of diffractometer; I_0 the intensity of incident per unit time; c the velocity of light; P_{rj} multiplicity factor; F_{rj} structure factor; θ_{rj} the diffraction angle; θ_α polarization angle; V is the diffracted volume of the sample; D_{rj} is the correction factor referring to line r of component j; X_j is the weight percentage of phase j; μ is the absorption factor; ρ_j is the density of phase j and V_{oj} is the unit cell volume of phase j. Various quantitative phase analysis methods have been developed based on this expression. These methods involve the measurement of integrated intensity ratios of nearby resolved lines with standard calibration mixtures with the proximity in angle compensating for angular-dependent aberrations.

After Rietveld addressed the problem of line overlap by considering the complete diffraction profile as a whole, it appears that the measured full profile can be replicated with calculated patterns based on crystal structure parameters and various corrections. In the Rietveld method, the diffraction intensity at a point i (in step-scanning mode) of a multiphase specimen is

expressed as:

$$Y_i = \sum_{j=1}^{n} S_j J_j A_j \sum_{r=1}^{k} L_r |F_r|^2 \Phi(2\theta_d - 2\theta_r) P_r + Y_{bi} \quad (2)$$

where, S_j is the scale factor of phase j; J_j is a function to model the effects of the surface roughness of phase j; A_j is the absorption factor; L_r contains the Lorenz factor, polarization and multiplicity factors of the Bragg reflection r (index hkl); Φ is the reflection profile function which approximates the effects of both instrumental and, possibly, specimen features; P_r is the preferred orientation function; F_r is the structure factor and Y_{bi} is the background contribution. The parameters in these functions can be continuously adjusted during the least-squares fitting procedure.

Comparing Equations 1 and 2, it can be shown that:

$$S_j = C X_j / \rho_j V_{oj}^2 \quad (3)$$

where, C is multiplier of constants that is correlated with the specimen and instrument. Equation 3 can be rewritten as:

$$X_j = S_j \rho_j V_{oj}^2 / C \quad (4)$$

It is a common practice to constrain the sum of the weight fractions to unity in a specimen; then the "relative" weight percentage of phase j can be determined by the Rietveld method using:

$$x_j = S_j \rho_j V_{oj}^2 \left/ \sum_{k=1}^{n} S_k \rho_k V_{oj}^2 \right. \quad (5)$$

where, ρ and V are constants for a particular phase, which are termed pattern intensity constants; S is the scale factor given by Rietveld analysis after various corrections. Commonly, ρ in Equation 5 is substituted by the calculated density. This substitution may introduce some errors; however, since in a specimen, all phases have nearly the same micro-structure, the error is not large. Thus, the relative weight percentage of identified phases can be accurately obtained by the Rietveld method without the use of a standard material.

If an internal standard phase s, which does not appear in the specimen, is added to the specimen prior to measurement, then the "absolute" weight percentage of phase j can be obtained from the following equation:

$$X_j = X_s S_j \rho_j V_{oj}^2 / S_s \rho_j V_{oj}^2 \quad (6)$$

Then, Equation 7 may be used to estimate the amount of minor phases and non-crystalline materials,

$$X_{Amorph\&Minor.} = 1 - \sum_{k=1}^{n} X_k \quad (7)$$

It is clear that there are some advantages in doing quantitative analysis by the X-ray powder diffraction full-pattern fitting Rietveld method: These advantages include:

(1) The utilization of the full diffraction profile and correction factors, thereby reducing the systematic effects of preferred orientation, extinction, absorption and instrumental configuration.

(2) A more efficient treatment (devolution) of the overlapping peaks, implying that patterns of greater complexity and containing broader peaks can be considered.

(3) The correct propagation of error into the quantitative analysis results, using the standard deviation of the scale factor for each phase, estimated in the least squares refinement.

(4) Relatively easy sample preparation.

(5) The ability to refine crystal-structure and peak profile parameters for the individual phases in the mixture, thereby providing "interactive" adjustments of their properties during the analysis.

3. Data analysis

The synthesized X-ray powder diffraction data were used as raw data to test the validity of this quantitative method in the analysis of the SiC polytype distributions since single phase SiC is very difficult to obtain. A convolution program was used to synthesize the diffraction pattern. In this program, the diffraction data calculated from crystal structure parameters were convoluted with instrumental broadening and size-strain broadening effects and also random noise was added. The instrumental profile parameters were obtained by fitting the step-scanned diffraction pattern of standard KCl powder obtained on a Rigaku Dmax/IIIB diffractometer. The domain size and micro-strain broadening effect was represented by using the Warren–Averbach method [4, 5]. The standard Wyckoff crystal structure data used in the synthesized program are listed in Table I. The data input into the program included the diffraction domain size, micro-strain, weight percentage and background parameter, diffraction angular range and step width. The resultant X-ray powder diffraction data can be compared with real diffraction data. In these calculations, the domain size and microstrain were 50 nm and 0.1%, respectively; the angular range was between 30–100° (2Θ) and the step width was 0.05° (2Θ).

TABLE I Crystal structure data for the SiC polytypes used in the calculations

Polytype	3C	4H	6H	15R
Space group	F-43 m	P6$_3$ mc	P6$_3$ mc	R3m
Cell parameters (nm)	$a = 0.43593$	$a = 0.30810$	$a = 0.30817$	$a = 0.3079$
		$c = 1.0061$	$c = 1.51183$	$c = 3.778$
Atom positions	Si	Si	Si 2a (0, 0, 0)	Si 3m (0, 0, 0)
	4a (0, 0, 0)	2a (0, 0, 0)	2b (0.6667, 0.3332, 0.1667)	(0, 0, 0.1332)
	C	2b(0.3332, 0.6667, 0.2500)	2b (0.3332, 0.6667, 0.3332)	(0, 0, 0.4000)
	4b (0.2500, 0.2500, 0.2500)	C		(0, 0, 0.6000)
		2a (0, 0, 0.1875)	C 2a (0, 0, 0.1254)	(0, 0, 0.8667)
		2b (0.3332, 0.6667, 0.4375)	2b (0.6667, 0.3332, 0.2919)	C also in '3m' with
			2b (0.3332, 0.6667, 0.4584)	$z_C = z_{Si} + 0.0500$

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Diffractometer: Rigaku Dmax/IIIB	Generator: 40 kV, 25 mA
Wavelength: CuK$_\alpha$	Diffracted beam monochromator: Graphite
Step: 0.04 ° (2Θ)	Collimators (DS, RS, SS, divergence slit, receiving slit and scattering slit): 1°, 0.6 mm, 1 °
Count time: 2s	Angular Range: 30–104 ° (2Θ)

The modified DBWS9411 program [6] was used to refine the synthesized data. A pseudo-Voight profile function was adopted to fit the experiment data and the range of calculated profile was defined to be $8H_k$. (H_k = the full width at half maximum of diffraction peak.) The background was refined with a 3rd order polynomial in 2Θ. Peaks below 45 ° were corrected for asymmetry. The calculation was terminated when all the calculated shifts were less than 10% of the standard deviation.

In all 38 parameters, including the instrumental, profile, cell parameters and scale factor were refined. In the first stage, only the scale factor and instrumental parameters were refined. When they had converged, the profile parameters were added. In the final refinements, the cell parameters were allowed to refine.

To verify this method, two specimens from the same sample of SiC that was thought to contain the 6H and 3C polytypes, were loaded in different sample holders and the X-ray powder diffraction data were recorded under conditions listed in Table II. The data reduction method was the same as that previously described.

4. Results and discussion
4.1. Synthesized data
The diffraction pattern is illustrated in Fig. 1. The R factors (numerical criteria of fit) are listed in Table III. From these figures and R factors, it can be seen that the Rietveld technique can successfully fit the severely overlapped peaks in the SiC diffraction pattern.
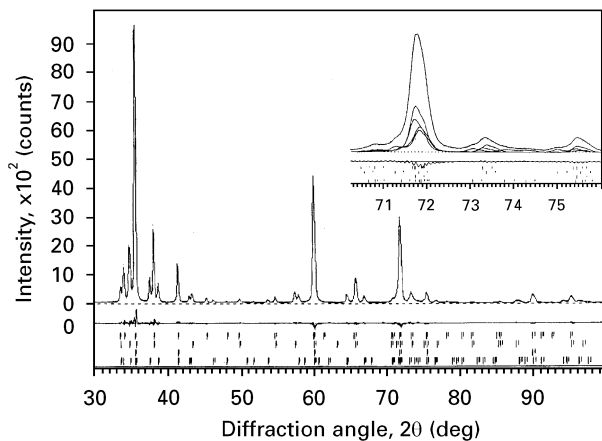

Figure 1 The calculated and synthesized X-ray diffraction patterns of experiment 2. The solid line is the calculated and the dotted line is the synthesized pattern with their deviations being shown beneath them. The vertical bars represent the peak positions. Part of the enlarged pattern is shown in the top right corner.

TABLE III The R factors for the calculated data

Experiment	1	2	3	4	5
R_{exp}	6.88	6.90	6.89	6.90	6.88
R_{wp}	9.01	8.29	8.52	8.41	8.89

Note: R_{exp} is the expected pattern R-factor;
R_{wp} is the weighted pattern R-factor.

Using the scale factors and cell parameters given by the Rietveld program, Equation 5 can be used to calculate the relative weight percentages of each detected polytype. The calculated results and weight percentages input into the synthesized program are listed in Table IV. The standard deviations in the weight percentages were also calculated based on the standard deviations of the scale factors.

From Table IV, one can clearly see that this quantitative analysis method can give an accurate account of the distribution of the SiC polytypes. The largest error occurred in the percentage of 4H in experiment 1, the relative error is 13%, but the absolute error is less than 2σ of its weight percentage; such a result can also be taken as being accurate.

The Rietveld quantitative analysis method also gives a reliable result of the SiC polytypes distribution. From the standard deviations listed in Table IV, it can be seen that the standard deviations of each polytype are consistent. The average standard deviations of the 6H, 4H, 3C and 15R polytypes are 0.63, 0.38, 0.39, and 0.41%, respectively. If 2σ is taken as the lower detection limit for which quantitative analysis method can give a reliable result, then the lower limit of detection by the Rietveld method for the above four polytypes, 6H, 4H, 3C and 15R are 1.26, 0.76, 0.78 and 0.82%, respectively.

4.2. Experimental SiC data
The X-ray diffraction pattern of one of the two specimens taken from the same material is shown in Fig. 2(a and b). The initial structural parameters were also taken from Table 1. When only the 6H and 3C polytypes were considered, the weighted R factor was 15.5% for specimen 1, and the residual difference between the simulated and calculated pattern showed the apparent appearance of the 15R polytype, as is illustrated in Fig. 2a. The crystal structure data for the 15R polytype was inputed into the Rietveld analysis program and an R_{wp} value of 12.9%, was obtained. When other polytypes, such as the 4H and 2H, were included in the refinement, the program gave minor minus scale factors, and the refinement did not converge easily. Therefore, the 6H, 3C and 15R are the

TABLE IV The relative weight percentages of four SiC polytypes, data in brackets are standard deviations (σ)

Experiment		6H	4H	3C	15R
1	Input (wt%)	74.94	4.08	0.98	20.01
	Calculated (wt%)	75.53 (0.68)	3.55 (0.34)	0.92 (0.35)	20.00 (0.44)
2	Input (wt%)	24.95	25.05	24.97	25.03
	Calculated (wt%)	25.15 (0.58)	24.49 (0.37)	25.60 (0.36)	24.76 (0.44)
3	Input (wt%)	49.95	30.06	14.98	5.01
	Calculated (wt%)	50.30 (0.65)	29.24 (0.41)	15.24 (0.41)	5.22 (0.43)
4	Input (wt%)	34.95	50.07	9.97	5.01
	Calculated (wt%)	35.51 (0.64)	49.19 (0.44)	10.40 (0.42)	4.90 (0.38)
5	Input (wt%)	55.94	2.07	29.97	13.02
	Calculated (wt%)	54.85 (0.60)	2.01 (0.33)	30.15 (0.42)	12.99 (0.36)

TABLE V The composition of the SiC material in terms of its polytypes, with the data in brackets being their standard deviations

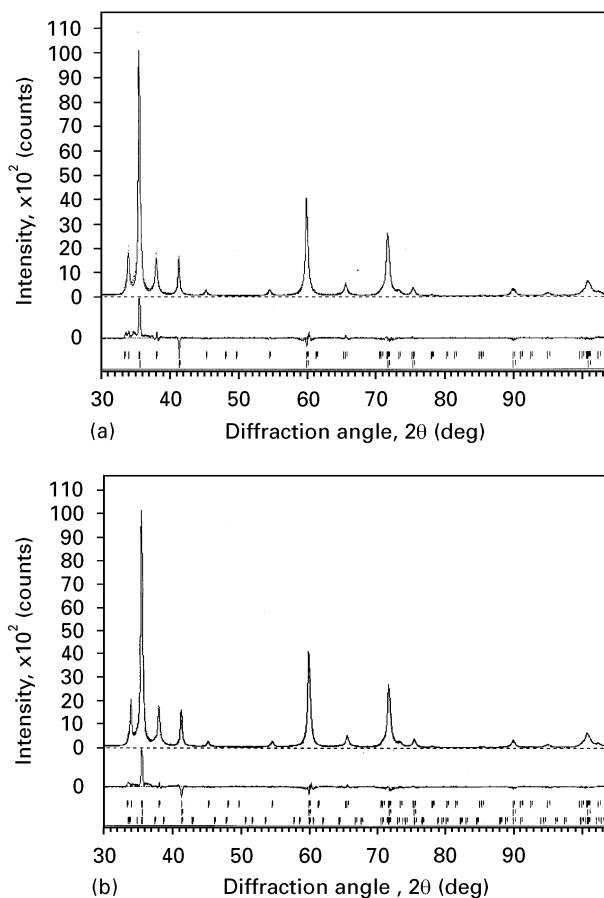| Specimen number	6H	3C	15R	R_{exp}	R_{wp}
1	54.4 (1.1)	30.58 (0.53)	14.84 (0.84)	6.16	12.9
2	53.4 (1.0)	31.09 (0.52)	15.47 (0.88)	6.05	12.6
Average	53.9 (1.1)	30.84 (0.53)	15.16 (0.86)		

Figure 2 The calculated and experimental X-ray diffraction patterns of specimen 1. (a) The diffraction pattern with only the 6H and 3C polytypes included in the refinement. (b) The diffraction pattern with three polytypes included in the refinement.

three polytypes considered to exist in this material. The final quantitative distributions of the polytypes in the two specimens are listed in Table V, along with their standard deviations.

From Fig. 2(a and b) one can see that apparent differences still exist at about 36° (2Θ), which is the main reflection of these polytypes. This difference may be due to stacking faults in the 3C polytype and the existence of higher order polytypes. For a detailed description, the reader is referred to the paper of Palosz *et al.* [7]. Because the higher order structures apparently form as the result of stacking faults introduced into the parent structures, the main reflections of these structures will overlap with those of the parent polytype and the differences will be relatively small. With the present experimental statistics, it is impossible to determine these minor high order polytypes.

5. Conclusions

The SiC polytypes distribution can be accurately and reliably determined by the X-ray powder diffraction full pattern fitting Rietveld method.

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