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Phase quantification of β-Si_3N_4/β-SiC mixtures by X-ray powder diffraction analysis*

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X-ray powder diffraction methods of phase quantification were adapted and compared to mixtures of β-Si_3N_4 and β-SiC. Multiline mean-normalized-intensity methods and whole pattern analysis (Rietveld) both have advantages and disadvantages over each other. Satisfactory results (less than 3% absolute deviation) can be achieved in minimal time using intensity normalization methods. Phase quantification using the Rietveld method requires significantly longer measuring time, evaluation time and expertise to obtain the same results.

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1. Introduction

Silicon carbide/silicon nitride composite materials are investigated by materials scientists for their improved mechanical properties over the single phases [1]. Superplastic behavior [2] and exceptional creep resistance [3] due to pinning of the β-Si_3N_4 grain boundaries by nano sized β-SiC particles have been reported. Furthermore, new processing techniques have been developed to produce silicon nitride/carbide composite materials, such as hybrid processing [4]. Quantitative phase analysis of SiC/Si_3N_4 mixtures is necessary to fully characterize these new ceramic materials.

A number of methods exist for quantitative phase composition analysis of silicon nitride powders. Gazzara and Messier [5] first proposed a multiline mean-normalized-intensity method using peak heights. Mencik *et al.* applied a reference-intensity-ratio (RIR) method [6]. Käll [7] studied the ratios of the α-Si_3N_4 (101), (210) and β-Si_3N_4 (102) and (210) lines using a defined set of peak heights and integrated intensities calculated from the Full Width at Half Maximum (FWHM). A calculation of the calibration constants and the influence of impurities is discussed. Li *et al.* [8, 9] extended Gazzara and Messier's work to incorporate integrated intensities and error analysis. They also compared their results to whole pattern (Rietveld) analysis. Devlin and Amin [10] proposed a reference intensity ratio (RIR) method circumventing the use of standards.

Ruska *et al.* [11] determined the quantitative composition of SiC polytypes, including polytype 3C (β-phase) by a combination of calculated X-ray intensities and experimental calibration curves.

Quantitative analysis of mixtures of silicon nitride and silicon carbide powders is hampered mainly by two factors: Extensive peak overlap, particularly concerning the β-SiC phase due to the small number of reflections and an extreme difference of peak shapes which can be troublesome even in whole pattern analysis.

The aim of this article is to adapt and assess existing methods of phase composition analysis to mixtures of β-Si_3N_4 and β-SiC powders. The accuracy of the results are compared while maintaining routine sample preparation techniques. No precautions against preferred orientation of the β-Si_3N_4 powders were taken. Any useful method of phase quantification would have to be applicable by non-specialists with average knowledge of X-ray diffraction techniques using standard equipment. Whole-pattern techniques, notably the Rietveld method, doubtlessly have many advantages over multiline techniques, but are usually much more complex and always more time consuming, not only in analysis, but in measurement in particular. In order to process large numbers of samples a quick and simple method of phase quantification is required.

2. Analytical method

2.1. Multiline mean-normalized-intensity method

The multiline mean-normalized-intensity (MNI) method is based on selecting a few well resolved peaks and then calculating the angle and structure related contributions to the integrated peak intensity. Thus, the unknown factor in the measured intensity is directly related to the volume fraction of the component phase. Following Li *et al.* [8] the integrated intensity for Bragg

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peak j of phase i in a Bragg-Brentano diffraction pattern can be expressed as

$$I_{ij} = \frac{C_0(mL_\mathrm{p}|F|^2)_{ij}\left(v_i/V_i^2\right)}{2\mu} \tag{1.1}$$

where C_0 is an instrument constant, m the multiplicity factor, L_p the Lorentz-polarisation factor, $|F|^2$ the structure amplitude, v_i the volume fraction of phase i in the mixture, V_i the unit-cell volume for phase i, and m the linear attenuation coefficient of the mixture. The integrated intensities need to be converted to normalized intensities (I_{ij}^n) according to

$$I_{ij}^n = \frac{I_{ij}}{R_{ij}} \tag{1.2}$$

where

$$R_{ij} = \frac{(mL_\mathrm{p}|F|^2)_{ij}}{V_i^2} \tag{1.3}$$

is the normalizing factor for line j of phase i. Finally, the volume fractions can be calculated (assuming no amorphous content):

$$v_i = \frac{\bar{I}_i^n}{\sum_p I_p^n} \tag{1.4}$$

As physical densities of β-$\mathrm{Si_3N_4}$ and β-SiC are nearly identical, the weight fractions were equated with volume fractions.

The structure factors were calculated anew to give a consistent set for each phase. The atomic coordinates from Rietveld analysis of the pure components (a minor amount of α-$\mathrm{Si_3N_4}$ is always present in β-$\mathrm{Si_3N_4}$ powders) were used in the calculations. The scattering factor data were taken from Hubbel *et al.* [12]. Anomalous dispersion correction was calculated with data according to Cromer [13]. The initial structure data for Rietveld analysis was taken from the ICSD database [14].

The reflections and R_{ij} used for α-$\mathrm{Si_3N_4}$, β-$\mathrm{Si_3N_4}$, β-SiC and Si are listed in Table I.

TABLE I Normalization factors, R_{ij}, used for multiline MNI calculations

Substance	*hkl*	2θ (Cu-K$_\alpha$)	R_{ij}
Si	111	28.5	35.1
	220	47.3	23.8
	311	56.2	14.3
β-SiC	111	35.7	37.0
	200	41.4	6.7
	220	60.0	17.1
	311	71.8	12.9
	222	75.5	1.9
β-$\mathrm{Si_3N_4}$	110	23.4	4.2
	200	27.1	11.9
	101	33.7	12.4
	210	36.1	11.4
α-$\mathrm{Si_3N_4}$	101	20.6	8.6
	110	22.9	3.7
	200	26.5	2.7
	201	31.0	8.4
	102	34.6	7.9
	210	35.3	7.9
	301	43.5	3.6

2.2. "Käll" method

Another method for the determination of β-SiC content in $\mathrm{Si_3N_4}$ is based on the work published by Käll [7]. For the clarity, the theoretical background is briefly repeated. In this method of quantitative analysis integrated intensities are used, which can be expressed by the formula:

$$I_{hkl} = \frac{N_{hkl}^o H_{hkl}}{(2^{2/3}-1)^{1/2}} = 1.30477\ N_{hkl}^o H_{hkl} \tag{2.1}$$

where N_{hkl}^o is the maximum peak height of reflection (hkl) that is corrected for background and overlaps, H_{hkl} is the full width of the reflection (hkl) at half its maximum height (FWHM). The corrected N_{hkl}^o values were calculated by solving the following linear equations:

$$\begin{aligned} f_{1,1}N_1^o + f_{2,1}N_1^o + \cdots + f_{n,1}N_n^o &= N_1, \\ f_{1,2}N_1^o + f_{2,2}N_2^o + \cdots + f_{n,2}N_n^o &= N_2, \\ \vdots \qquad\qquad \vdots \qquad\qquad &\vdots \\ f_{1,n}N_1^o + f_{2,n}N_2^o + \cdots + f_{n,n}N_n^o &= N_n \end{aligned} \tag{2.2}$$

where $f_{i,j}$ are the overlapping factors and N_j are the measured peak heights corrected for the background (this correction was done by the software of X-ray diffractometer). The overlapping factor $f_{i,j}$ of peak i on to peak j was calculated according to

$$f_{ij} = \left(1 + k_i^2|\theta_j - \theta_i|^2\right)^{-3/2} \tag{2.3}$$

where k is equal to

$$k = \frac{2(2^{2/3}-1)^{1/2}}{H_{hkl}} = \frac{1.53284}{H_{hkl}}. \tag{2.4}$$

In (2.3) i and j denote the indices of the overlapping reflections, and $|\theta_j - \theta_i|$ represents the distance between the two peaks. The intensity ratios were calculated according

$$Q = \frac{I_\mathrm{c}}{(I_\mathrm{n} + I_\mathrm{c})} \tag{2.5}$$

where the indices n and c denote two different phases, i.e. n represents silicon nitride (β-$\mathrm{Si_3N_4}$) and c silicon carbide (β-SiC), respectively. The intensity of (hkl) reflection from the phase j can be also expressed as

$$I_{j(hkl)} = \frac{K_{j(hkl)}w_j}{\sum \mu_{\mathrm{m},i} w_i} \tag{2.6}$$

where $K_{j(hkl)}$ is a constant for the reflection (hkl), w_i is the weight fraction of the phase $i (i = 1, 2, \ldots, n)$ and $\mu_{\mathrm{m},i}$ is the mass absorption coefficient of the phase i. The $K_{j(hkl)}$ constant for single j phase is equal to

$$K_{j(hkl)} = \frac{C_0 L_{\mathrm{p}m}|F_{hkl}|^2 e^{-2M}}{\rho V^2} \tag{2.7}$$

where C_0 is the scale constant, m the multiplicity of the (hkl) reflection, L_p the Lorentz- and polarization factors, F the structure factor, e^{-2M} the Debye-Waller temperature factor, V the cell volume and ρ the density ($\rho = \mu/\mu_{\mathrm{m}}$, ratio of the linear and mass absorption coefficients). The intensity normalization step is thus similar to that of Li *et al.* [8], the $K_{j(hkl)}$ can easily be converted to the R_{ij} of Equation 1.3. After substitution of (2.6) into (2.5) this equation can be modified to the formula:

$$Q = \frac{w_c \sum K_{c,i}}{(w_c \sum K_{c,i} + w_n \sum K_{n,i})} \tag{2.8}$$

After dividing the numerator and the denominator by $\sum K_{n,i}$ the equation simplifies to

$$Q = \frac{K w_c}{(K w_c + w_n)} \tag{2.9}$$

where $K = \sum K_{c,i} / \sum K_{n,i}$. Assuming $w_c + w_n = 1$, the weight fraction of SiC can be calculated according to

$$w_c = \frac{Q}{(K(1 - Q) + Q)} \tag{2.10}$$

The value of Q is calculated from (2.5).

2.3. Rietveld method

The Rietveld method and its applications to quantitative analysis have been well described in the literature (e.g. Bish and Howard [15], Hill [16]). Briefly, the intensity of a diffracted X-ray beam using reflection geometry is defined as

$$I_{hkl} = C\left(\frac{1}{2}\mu_{\mathrm{m}}\right) R_{hkl} \tag{2.11}$$

where C is a constant depending on the primary beam intensity. R_{hkl} varies with the crystal structure and the diffraction angle. The term μ_{m} describes the linear absorption coefficient of the mixture. In a powder mixture, the contribution of phase α to the integrated intensity I_{hkl} is given by

$$I_{\alpha,hkl} = \frac{W_\alpha \rho_{\mathrm{m}}}{\rho_\alpha} C\left(\frac{1}{2}\mu_{\mathrm{m}}\right) R_{hkl} \tag{2.12}$$

W_α is the weight fraction of phase α. The scale factor of phase α derived from Rietveld analysis S_α is

$$S_\alpha = \frac{W_\alpha \rho_{\mathrm{m}}}{\rho_\alpha} C\left(\frac{1}{2}\mu_{\mathrm{m}}\right) \tag{2.13}$$

In Equation 2.13 both W_α and μ_{m} are unknowns, but the latter can be eliminated by the requirement that the sum of all weight fractions must be equal to unity. For a two-phase mixture we can write

$$W_\alpha = \frac{W_\alpha}{W_\alpha + W_\beta} \tag{2.14}$$

By combining (2.13) and (2.14) we obtain the weight fraction of the ith phase in a mixture of n phases

$$W_i = \frac{S_i \rho_i}{\sum_{j=1}^{n} S_j \rho_j} \tag{2.15}$$

To sum up, the three methods each have relative merits. The MNI method can be performed very quickly on data measured from approximately 20–65° 2θ (Cu-K_α), provided that integrated peak intensities can be readily obtained. Peak intensities are replaced by peak widths in the "Käll" method, at the expense of a few extra calculations. Although some Rietveld analysis programs automatically generate the weight fraction in the output, it is far from trivial to setup and operate a stable Rietveld calculation. Data must be collected over a wide angular range in order to avoid indeterminacy of the least squares calculation.

3. Experimental

In sintered samples of β-$\mathrm{Si_3N_4}$/β-SiC materials the silicon nitride tends to form elongated grains which can result in preferred orientation of the crystals. For this reason, two types of commercial, additive-free β-$\mathrm{Si_3N_4}$ materials were used: "BS" crystals are predominantly equiaxed, recrystallized from α-$\mathrm{Si_3N_4}$ which in turn is produced by direct nitridation of silicon (grade SN-BS, Denka, Japan). "SHS" powder was produced by self-propagation high-temperature synthesis (Institute of Macrokinetics, Chernogolovka, Russia). The grains of the "SHS" powder are elongated up to 20 μm in length [17]. Silicon carbide was commercial "Superior Graphite" (Grade 059). Grain sizes were determined by SEM to be approximately 1 μm for "BS" β-$\mathrm{Si_3N_4}$ and β-SiC.

The powder mixtures were prepared by homogenizing the weighed components in alcohol for 10 min in an ultrasonic bath, then 16 h on a rolling homogenizer. Afterwards the powders were homogenized in the ultrasonic bath again for 5 minutes and dried for 2 to 3 h. Powders were packed into the sample holder cavity and pressed with a flat glass plate to ensure a flat sample surface. Keeping routine preparation techniques in mind, no special measures were taken to prevent preferred orientation. Furthermore, the effects of sample transparency which can lead to erroneous intensity values and peak shifts in light element materials on a Bragg-Brentano diffractometer were ignored.

Two series of powder mixtures with variable silicon carbide contents were prepared—series "A" with "SHS" silicon nitride and series "B" with "BS" silicon nitride. Both series were measured in Bragg-Brentano geometry on a standard powder diffractometer (Siemens D5000, Karlsruhe) using Cu K_α radiation. The measuring parameters were varied to simulate a quick routine measurement (series A) and a "normal" routine measurement (series B). The data were collected over an angular range of 20 to 65° 2θ with a step interval of 0.03° 2θ and 4 s per step for series A, series B used a step interval of 0.02° 2θ and 2 s per step. Sample holder cavity depths were approximately

3 mm for series A and 1 mm for series B. Irradiated sample volumes were estimated to be equal within a series. The divergence slits were set to 0.5° for series A and 0.27° for series B.

The β-Si_3N_4 reflections used for the analysis are the same as reported by Gazzara and Messier [5]. The case of β-SiC is more difficult, because the (200) reflection has a d-value identical to the β-Si_3N_4 (201). The β-SiC (111) and (220) reflections are somewhat overlapped, but are either sufficiently resolved by the profile analysis software, or the intensity of the overlapping reflection can be neglected. All other SiC reflections also suffer from peak overlap and low relative intensity.

Integrated intensities were determined by profile fitting using the "PROFILE" software of Siemens. A split-Pearson-VII function was applied to both silicon nitride and silicon carbide reflections. Rietveld analyses were performed using the GSAS package [18].

A minor amount of α-Si_3N_4 was present in the β-Si_3N_4 powders. A quantitative analysis following the MNI-method of Gazzara and Messier [5] and Li *et al.* [8] as well as Rietveld analysis gave a weight fraction of approximately 0.10 α-Si_3N_4. This value was held constant in the following MNI calculations.

Contrary to mixtures of the α and β phases of Si_3N_4, the accuracy of a quantitative phase analysis can be estimated by comparing the results determined by experiment to the amounts weighed. On the other hand, an error analysis was omitted because only one Si peak and two SiC peaks could be seriously considered.

Measurements for Rietveld analysis were optimized to obtain the best possible data set. A powder diffractometer in Debye-Scherrer transmission geometry (Stoe, Darmstadt) was selected. A primary beam Ge focusing monochromator delivered Cu-Kα_1 radiation. The sample was rotated during measurement. The data were collected on a position-sensitive detector.

4. Results and discussion

4.1. MNI method

It is common among papers on quantitative analysis to present results in the form of absolute error. Figs 1 and 2 plot the absolute error defined by the difference between the weighed and determined amount, versus the weight fraction of SiC for series A and B, respectively. The main differences between the A and B series are grain shape and measuring time. The B series silicon nitride crystals are equiaxed and the powder mixtures were measured longer. These parameters do not seem to greatly influence the quantification results particularly because a multi-line method is being used. The relative errors are given for the A series in Fig. 3. As it would be expected, the relative error increases considerably for low values of SiC. This can be attributed mainly to the problem of determining the integrated intensity. Due to the super-lorentzian peak shape [19], the peak is almost completely dissolved into the background for weight fractions of 0.10 or less. In this case, the silicon carbide (220) peak could not be detected at 5 wt% and below. Because of the short measuring time of the series B data it was not reasonable to determine the β-SiC weight fraction below 0.15–0.20. However, Fig. 4 makes clear that it is quite difficult to determine a low SiC phase content by any method, since 5 wt% is close to the detection limit.

In particular, Fig. 3 shows that it is possible to reproducibly estimate the phase content of β-SiC in β-Si_3N_4 within 3% above a silicon carbide weight fraction of 0.2.

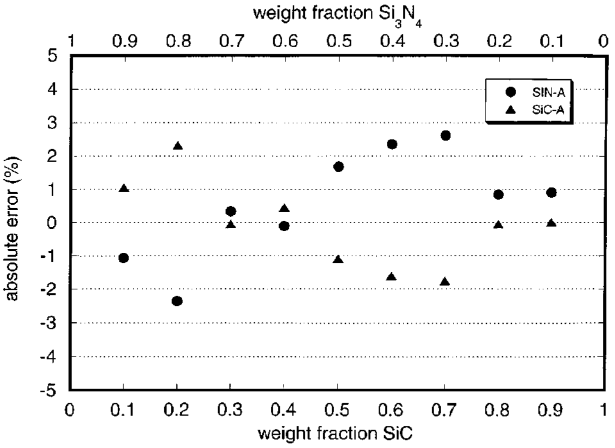

Figure 1 Absolute error of calculated weight fractions, series A. Results of multline MNI calculations.

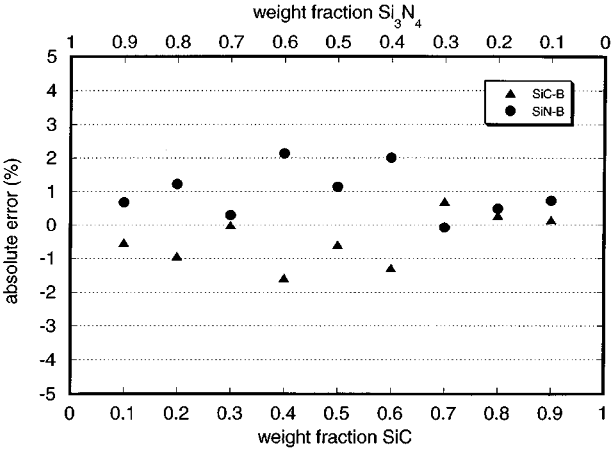

Figure 2 Absolute error of calculated weight fractions, series B. Results of multline MNI calculations.

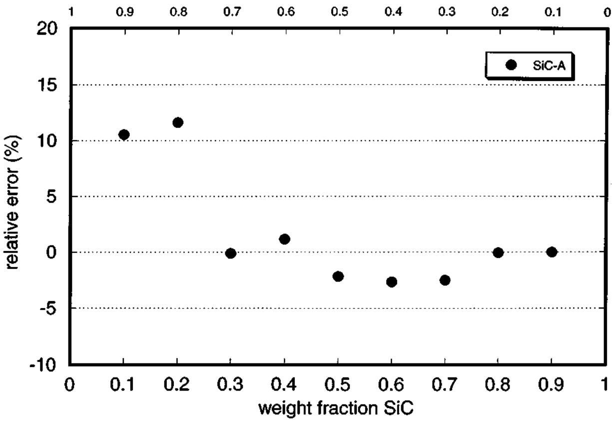

Figure 3 Relative error of calculated weight fraction for β-SiC, series A. Results of multline MNI calculations.

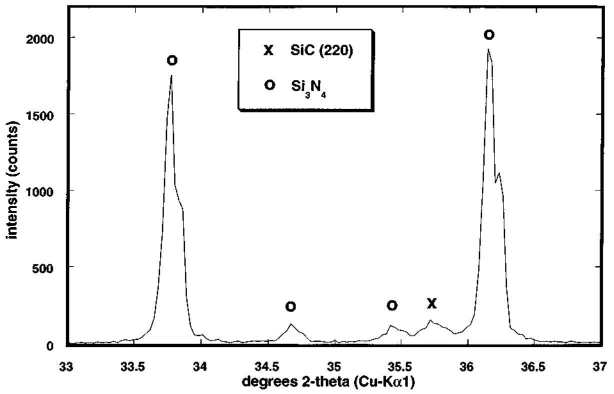

Figure 4 X-ray diffraction pattern of β-SiC (220) at 10% weight fraction.

4.2. "Käll" method

In this part of our work the data from series A, and the following reflections have been used for calculations: (101) and (210) for β-Si_3N_4 and (111) for β-SiC. The advantage is that the XRD measurement need only be done for a narrow angle range $2\theta \in \langle 33^\circ; 37^\circ \rangle$. For these peaks the intensity ratio is

$$Q = \frac{I_{111}}{(I_{111} + I_{101} + I_{210})}.$$

The data required for the calculation of integrated intensities according to (2.1), i.e. H_{hkl}, $|\theta_j - \theta_i|$ and N_{hkl} were determined from the X-ray diffractogram. H_{hkl} was measured in a light microscope equipped with a micrometer scale. If available, this operation also can be done by XRD profile software.

Based on measured data the overlapping factors were calculated and are listed in Table II. Except for diagonal overlapping factors, which are equal to unity, only the $f_{111,210}$ and $f_{210,111}$ overlapping factors were included into the calculations in Equation 2.2, because the influence of the others ($f_{i,j} < 10^{-3}$) on final values of integrated intensities was negligible. Finally, the β-SiC content was calculated according to Equation 2.10, with the value of $K = 1.56606$ on the base of the data listed in Table III. It must be remarked that the calculated K_i values are valid only for Bragg-Brentano powder diffractometer data. The calculated values were compared with the real β-SiC content added, and the results are shown in Fig. 5. As can be seen, there is a good agreement between calculated and actual β-SiC content, and the accuracy is in the range of ±3 wt%. If only peak heights corrected for background were used, the deviation was ±5.5 wt%, what is acceptable for rough estimation of β-SiC content in β-Si_3N_4. It must be noticed, that this method may be used only for well crystallized materials, without amorphous phase and α-SiC. Use of powdered samples is recommended, because e.g. in bulk hot pressed materials, the preferred orientation of elongated β-Si_3N_4 grains is very strong and noticably influences the peak intensity ratios. If the powder mixture contains α-Si_3N_4, (102) and (210) reflections of this phase should be included into the calculations as described by Käll [7].

TABLE II Average overlapping factors $f_{i,j}$, used in calculations of peak widths (Käll method)

f_{ij}	Value
$f_{111,101}$	3.92×10^{-4}
$f_{111,210}$	3.70×10^{-2}
$f_{101,111}$	9.13×10^{-5}
$f_{101,210}$	5.20×10^{-5}
$f_{210,111}$	1.25×10^{-2}
$f_{210,101}$	6.89×10^{-5}

TABLE III Theoretically calculated $K_{(hkl)}$ values for β-Si_3N_4 and β-SiC, including densities (ρ) and linear absorption coefficients (μ) used for calculation of $K_{(hkl)}$ (Käll method) [20]

Parameter	β-SiC	β-Si_3N_4
ρ ($g \cdot cm^{-3}$)	3.216	3.201
μ (cm^{-1})	141.112	126.299
$K_{(111)}$	259690.5	—
$K_{(101)}$	—	84901.2
$K_{(210)}$	—	80923.1

TABLE IV Absolute difference of calculated minus given weight fraction analyzed by Rietveld method

Parameter	50/50-mixture	70/30-mixture
Counts, β-Si_3N_4 (200)	9000	2300
β-Si_3N_4	−1.3%	+3.4%
β-SiC	+1.8%	−3.0%

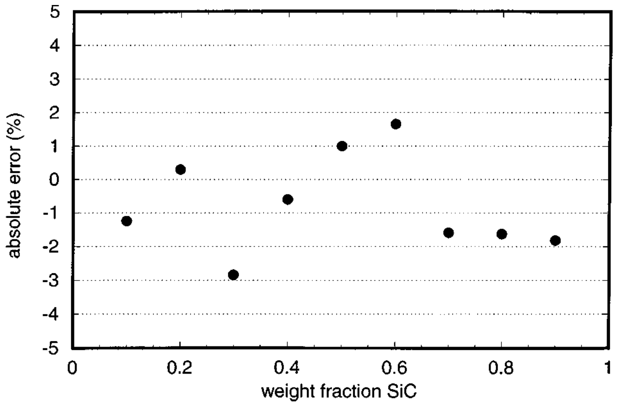

Figure 5 Comparison of calculated and weighed-in fraction of β-SiC (Käll method).

4.3. Rietveld method

Two measurements were made on the Stoe diffractometer which differ by the phase composition and duration of measurement. A mixture of 50 wt% silicon carbide and 50 wt% silicon nitride was measured so that approximately 9000 counts were detected for the highest peak. Approximately 2300 counts were detected for a mixture with 30 wt% silicon carbide. It should be noted that different data sets were used for MNI/Käll and Rietveld methods because the requirements are much higher in the case of Rietveld analysis. On the other hand, use of transmission geometry data sets are not recommended for use with the MNI method due to the uncertainty of the absorption coefficients.

The results from the Rietveld analysis are given in Table IV. Obviously, the quality of a Rietveld refinement strongly depends on the quality of the data and for a precise measurement the error is less than ±2 wt%. When using a data set with 2300 counts for the highest peak, as with the 70–30 mixture data used for Rietveld analysis, the quality of the measurement is significantly greater than the corresponding data set used for the MNI method in series A (approximately 1600 counts for the most intense peak). The results, however, are significantly worse (cf. Table IV).

5. Conclusions

In this paper we have presented two methods of quantitative phase analysis by X-ray diffraction which can be applied without the experience and knowledge of a professional crystallographer. In addition, we have shown that measuring time can be significantly reduced as compared to the quality of data that would be necessary for whole pattern analysis. The multiline quantification methods give satisfactory results in a very short time with minimal expertise necessary. Both the MNI method and the "Käll" method allow a phase quantification to within 3% absolute of the true value. This is expected since the MNI and "Käll" methods differ only slightly in their peak normalization steps. The "Käll" method has the advantage of being truly independent of in-depth crystallographic expertise. Peak widths are used instead of peak areas and only a very narrow range of 4° 2θ (using Cu-K_α) need actually be measured. However, unexpected additional phases might escape detection when only a very narrow range or a few selected peaks are investigated. The limits of multiline methods described above are reached when intrinsic problems, such as the inability to determine the peak area of SiC reflections at very low phase contents (below 10 wt%), are encountered. This can only be solved by allotting a disproportionately large amount of measuring time. In spite of the disadvantages, the Rietveld method has the advantage of using the entire diffraction profile for quantification, thus making it easier to detect unexpected phases.

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