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Determination of the ratios of polytypes in a silicon carbide grit using neutron diffraction

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The distribution of polytypes in a sample of silicon carbide has been measured by the technique of neutron powder diffraction profile analysis. Three polytypes are shown to be present and their relative proportions have been calculated. The neutron technique was used because it was desired to examine the bulk properties of the sample and to use large (~ 1 cm) samples.

1. Introduction

Silicon carbide shows a pronounced tendency to crystallize into a number of different structures called polytypes. The proportions of these polytypes seems to depend on the exact method of manufacture and the results are often more of an art than a science. Although not the only substance to form polytypes, it is unique because of the strong dependence of its electrical properties on the polytype.

These electrical properties show that SiC could be used as a semi-conductor material, with a number of outstanding advantages such as high voltage and high temperature operation and an ability to emit blue light. However, because of the difficulty in obtaining large supplies of identical crystals of a known polytype, development has been slow [1].

SiC forms its many polytypes by variations in layer stacking. Essentially there are three layer types and different polytypes are formed by different repeat distances in the stacking procedure. For example the cubic 3C* phase has stacking in the ABC notation as follows, ABC, ABC, whereas the hexagonal 6H polytype has an ABC, ACB, ABC ACB structure. The immediate consequence is that the reflections from individual polytypes are very often coincident. For example if only the 3C and 4H phases are present all the major 3C lines coincide with 4H lines. Quantitative measurements, therefore, must be made by comparing the measured intensities with those calculated from a theoretical model. This is relatively straightforward for the neutrons diffraction case since the scattering factors are isotropic and the absorption is low (typically μ, the linear absorption coefficient of the sample, is of the order of 0.1 cm^{-1}). The low absorption also makes it possible to examine the "interior" of a sample rather than the surface layers as in the X-ray case.

2. Method of analysis

The neutron diffraction patterns were obtained from a conventional neutron powder diffractometer, DELILAH, [2] located on the 5 MW reactor HERALD at AWRE Aldermaston. The diffractometer is controlled by a small computer and is entirely automatic in operation [3].

About 2.5 g of powdered sample were put into a thin walled vanadium tube and mounted on the diffractometer. Vanadium has a near zero coherent scattering cross-section for neutrons and its use obviates any contaminating lines from the sample-holder. A typical scan is shown in Fig. 1a.

Because in neutron diffraction the relative peak intensities can be calculated very accurately and the diffraction peaks shapes are almost exactly Gaussian, it is quite feasible to construct a theoretical spectrum from a given structure. By comparing this theoretical spectrum with the measured, the accuracy of a particular model can be calculated. A program using this method has been developed at AWRE to determine the proportions of chemical phases present. It is

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*Using Ramsdell's notation.

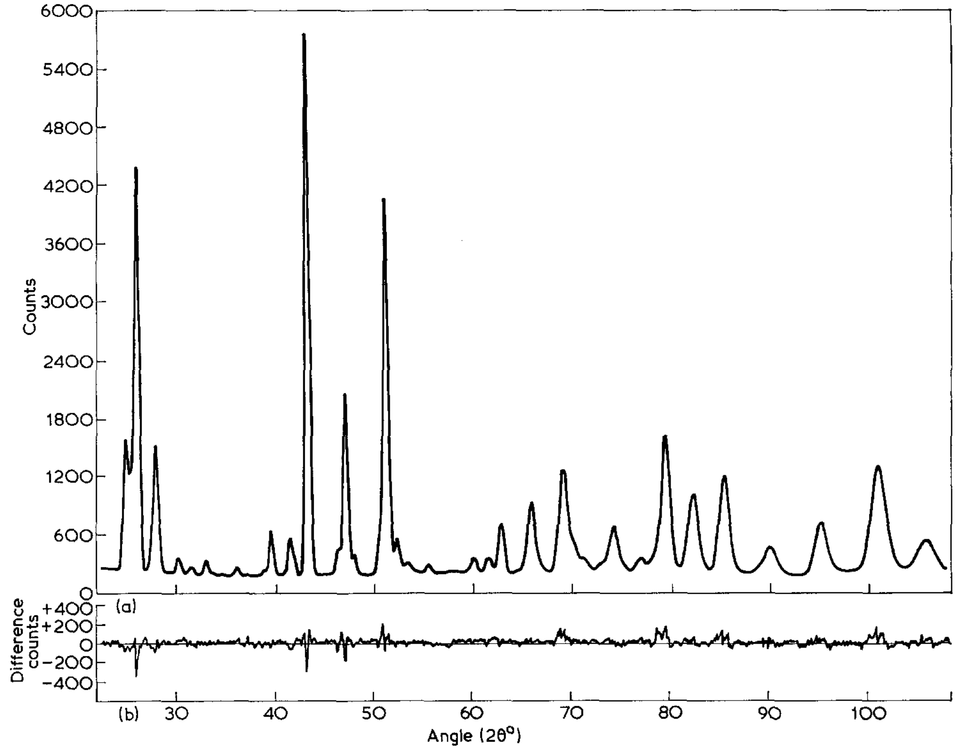

Figure 1 (a) Calculated powder profile for the four phase model of SiC. (b) Difference between calculated profile and experimental results.

similar in concept to the method used by Rietveld [4] for single phase material, although developed independently, and uses a least squares fitting method to produce the best fit from the given number of phases. As the prime purpose of the program is phase analysis, no attempt was made to incorporate a least squares structure refinement.

Like other profile powder techniques, an approximate idea of the structure and polytypes present is required before starting the analysis. The structures used for the polytypes of SiC were basically those given by Wyckoff [5], though modification of cell sizes was necessary to produce a good fit. As more than 100 polytypes have been noted for SiC it was necessary to restrict the number used in the model. Apart from the cubic 3C modification which is now generally accepted as a metastable low temperature phase, most observed structures seem to be based on 4H, 6H and 15R polytypes [6]. More recently, structures based on the 21R and 33R modifications have also been observed [7] although they are comparatively rare.

Initially, therefore, the four most common polytypes, 3C, 4H, 6H and 15R were used for the model. This produced an excellent fit to the experimental data as is shown in Fig. 1b. It should be noted that, because of the close correspondence of the experimental and theoretical spectra, it is preferable to show the goodness of the fit by a difference plot, which has the effect of magnifying any errors.

Attempts to use six phases by the inclusion of the 21R and 33R modifications resulted in a best fit with a small negative amount of 3C, a near zero amount of 33R and 11 % of 21R. The mean square error was slightly worse. Close observation of the theoretical spectra showed that some fine superstructure should be present in this case, an example is shown in Fig. 2, which was not present in the experimental data. It was therefore concluded that the 21R polytype was not present in any significant amount. This shows the possible danger in blindly accepting the results of least squares fitting without close examination.

It is interesting to compare the present results

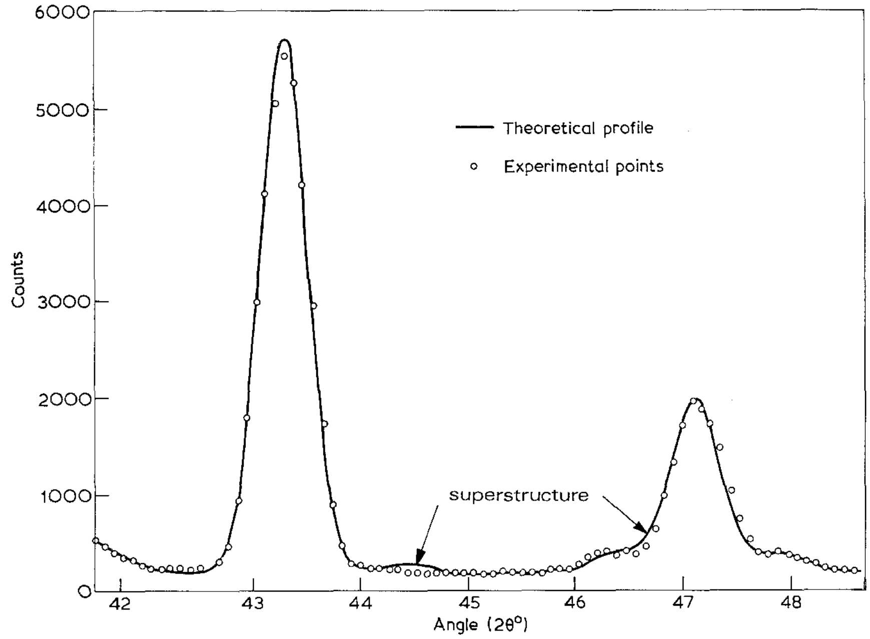

Figure 2 Part of the powder profile for a six-phase model showing typical superstructure due to 11% of the 21R polytype.

with those given by Dubey *et al.* [6] and Jagodzinski and Arnold [8] both of these being measured by X-rays. In the case of Dubey, the percentages present are the frequency of occurrence of polytypes crystals rather than the actual molecular weight ratio. It should be noted that for our results the errors quoted are those due to the counting statistics of the data.

The original cell size parameters were based on those given by Taylor and Jones [9] for 3C and 6H, namely, $a_0 = 3.0806$, $c_0 = 15.1173$. Other hexagonal modifications were assumed to have similar a_0 values and a c_0 value scaled up by the molecular ratio. During refinement of the data it was found that the best fit was obtained with a hexagonal cell a_0 of 3.0771 ± 0.0003 Å and a c_0 of 5.0333 ± 0.0005 Å × $M/2$ where M is the number of molecules in the hexagonal cell. These values are referred to a nickel calibration sample with a value for the nickel a_0 of 3.5239 Å.

3. Discussion

A very large number of polytypes of SiC exist; all, like those considered here, due to variations in the stacking of planes layers in the C-direction. We must emphasize, therefore, that powder diffraction does not give unequivocal results and, whereas it is possible to identify a particular

TABLE I Comparison of present measurement with those of Jagodzinski and Arnold [8] and Dubey *et al.* [7]

Polytype	Present paper	Dubey *et al.*	Jagodzinski and Arnold's analysis of SiC in zones of an arc furnace					
			Hot 1	2	3	4	5	Cold 6
3C	0.2 ± 0.3		29	29	30	33	28	56
4H	19.7 ± 0.5	1	—	—	1	9	6	4
6H	63.7 ± 0.5	75	71	72	65	44	59	41
15R	16.3 ± 0.3	15	—	—	3	14	8	8
21R	< 1	4	—					
33R	< 1	2	—					

model with the experimental data, it is not the only solution. The model used here is based on the six simplest polytypes initially and on four of the six after refinement. It is quite possible that small proportions of the higher order polytypes do exist in the sample we measured. However, because these higher order structures seem to form as the result of stacking faults introduced into the parent structure, the main reflections will coincide with those of the parent and the differences will be relatively small. With the present experimental statistics it is impossible to observe these differences for a few per cent of the higher order polytypes, which as a result will be included with the parent structure.

Our model differs markedly from that of Jagodzinski and Arnold in showing no proportion of the cubic 3C phase or anyway less than 1%. Whilst the 3C phase is difficult to detect since there are no reflections free from contamination, we are confident that the diffraction patterns indicate the lack of it in this sample. This is perhaps surprising because the 3C phase is the simplest phase and might be expected to be present. However, if as Knippenberg argues [10] the 3C phase is metastable then its presence would be very dependent on the exact method of manufacture.

In conclusion the results shown above indicate that this type of analysis is quite feasible using neutron diffraction. Although the available flux is very much lower when using neutron *vis à vis* X-rays, the use of the former does have some specific advantages. Firstly the scattering process is essentially isotropic. There are, therefore, no angular dependent terms in the structure factors, which leads to considerable simplification in calculation. Secondly, the absorption is usually low in the neutron case and extinction effects are negligible in the powder case. It is this simplicity that enables the profile analysis method to be readily used. Moreover, large samples can be analysed and effects due to granularity and porosity of the sample and differences between the surface and the interior of the sample are eliminated. Thus the technique lends itself to the measurement of polytypes in fabricated components.

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