

EVOLUTION OF DISORDERING IN SiC UPON SINTERING; PHASE ANALYSIS OF SiC BY RIETVELD METHOD WITH APPLICATION OF NEUTRON AND X-RAY DIFFRACTION

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Neutron and X-ray diffraction patterns of α and β powders as well as of sintered SiC were analysed by a multiphase Rietveld method. It is shown that structural models combined of large period polytypes can be used to approximate the disordering of these polytype structures. The hexagonality of the samples could be terminated with reproducibility 1-2% using different combinations of large-period polytypes. It follows that the usual classification into α and β SiC is an oversimplification. The polytype behaviour of SiC powders and the role of twinning of cubic layer stackings is discussed. Distribution functions of stacking sequences of different length in α and β phases are derived.

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1. Introduction

Silicon carbide is a prominent polytype material and occurs in a number of different structural modifications: periodic and non-periodic (disordered) [1]. It is usually classified as α and β SiC. Here β represents a cubic phase and α includes various hexagonal and rhombohedral polytypes. For the α phase the contribution of a few basic polytypes: 2H, 4H, 6H and 15R and occasionally disordering of the

structures was discussed [2-6]. Electron-microscopic studies of individual powder grains show however that there is a variety of multilayer structures with very large periods coexisting with the basic structures [5, 6].

Powder diffraction patterns show a small number of dominant reflexions which can all be attributed to the basic structures. It is observed, however, that these reflexions are often broadened with characteristic "diffuse peaks" around some specific reflexions. These diffuse peaks indicate that the structure is disordered and inhomogeneous. Structural changes of polytype structures during sintering are described in the literature, e.g. [4-6].

This work presents an application of the Rietveld method [7, 8] to the analysis of disordered polytype structures of SiC and to the examination of the structural changes occurring in α and β powders during sintering. Neutron and X-ray diffraction gives information about the average structure (averaged over all powder grains) and not about local variations of the layer stackings within individual powder grains. (Preliminary results of this work were presented at the International Workshop of the Rietveld Method, Petten, 1989.)

2. Experimental

Neutron data were collected on the MAN-I powder diffractometer at the FRM reactor in Garching with a Cu(220) monochromator, $\lambda = 1.075 \text{ \AA}$ in a step scan mode of interval $0.1^\circ 2\theta$. Samples were in the form of cylinders 10-15 mm in diameter, 10-20 mm high.

X-ray data were collected on a STOE-type diffractometer with a curved Ge(111) monochromator, and with flat plate of samples coated on foil in transmission geometry and a scintillation counter as a detector. The resulting divergences were 0.5° horizontally and 1.46° vertically. Data were collected in a step scan mode at intervals 0.02 and $0.1 2\theta$. The samples are specified in Table I.

TABLE I

Samples specification.

No.	Type	Source
I	β powder	STARCK
II	α powder	STARCK
III	ceramics	
	α sintered	STARCK
IV	ceramics	
	β sintered	STARCK
V	β powder	combustion (SHS)
VI	β powder	plasma spraying

3. Characteristics of silicon carbide structure

From single crystal work it is known that there is an almost unlimited number of different structural modifications of SiC: one *cubic* structure (3C) and variety of *hexagonal* (nH) and *rhombohedral* ($3nR$) polytypes and also non-periodic disordered structures [1]. In a first approximation it is assumed that the interlayer spacing (the distance between two subsequent layers Si-C) is preserved (about 2.52 Å) independent of the stacking, i.e. the layers are always closed packed.

Although there is no clear evidence that some specific layer stackings are more stable than others, it is generally agreed that the layer stackings occurring more frequently than others are the more stable ones. These structures are called basic polytypes: 3C — cubic, 2H, 4H and 6H — hexagonal and 15R — rhombohedral.

According to commonly used α - β classification of SiC materials there *should* be the difference between α and β related to symmetry between 3C as cubic i.e. fully isotropic and all other polytype structures which are anisotropic. This classification of SiC powders into β as cubic (3C) and α for others is often misleading. As known from single crystal work and from electron-microscopical observations the pure cubic structure occurs in single crystals only occasionally. It is usually twinned and the same behaviour is expected in powder samples. 3C occurs in syntactic coalescence with hexagonal and rhombohedral polytypes suggesting that there is a continuous transition between cubic 3C and other polytype modifications of SiC.

A uniform description of the periodic and disordered structures of SiC can be given with the use of Zhdanov and hc-notations (Fig. 1) [1]. A single Zhdanov

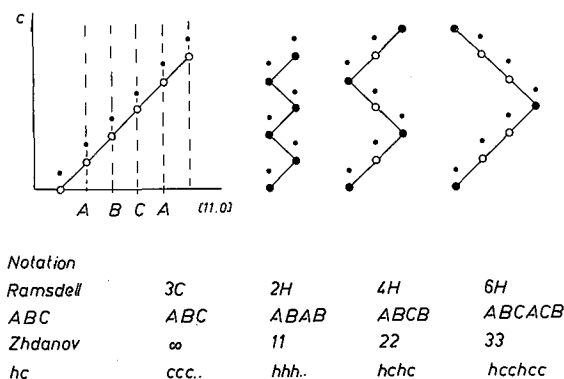


Fig. 1. Stacking sequences of Si-C layers in the (110) plane of the polytypes 2H, 3C, 4H, 6H.

number n_i represents one domain of the 3C structure and a change of the stacking from (-) to (+) is equivalent to twinning of the 3C structure. According to the hc notation a single SiC layer can have either hexagonal h or cubic c surrounding. A single domain of 3C is a sequence of c layers and one h layer. A multidomain structure is then combined of blocks of c layers separated by h layers which occur at the interdomain 3C(+)/3C(-) boundaries.

From geometrical conditions of close packing there are no restrictions on the relative content of cubic- and hexagonal-like layer stackings. Percent of hexagonal h layers is called *hexagonality* and this value for particular structure can be within the range 0–100 %h.

4. Data evaluation

Silicon carbide can be considered as either being combined of pure polytypes (periodic structures) or as a disordered structure which is non-periodic. Note that disordering related to a larger volume does not exclude periodic ordering (i.e. the occurrence of various polytypes) in small parts of the volume, e.g. in single powder grains.

Powder patterns will be very similar for (i) a single very large period polytype, (ii) a combination of several polytypes (a multiphase system) and (iii) randomly disordered structures. When examining polytype structure of SiC one has to take into account that the lattice constant a is very similar for all polytype structures and the constant c is a multiple of the invariant interlayer distance c_0 which, in fact, vary very little from polytype to polytype, see e.g. [9–13]. Therefore, the reflexions of individual polytypes occur at similar positions and are often indistinguishable.

In the diffraction patterns of (i) and (ii) there will be very strong overlap of individual (small) reflexions which combine into broad lines looking like single (broadened) reflexions of a small period polytype sitting on a diffuse peak. Similar broadening and diffuse tails of the reflexions will be observed for randomly disordered structures (iii). Note that disordering is in one dimension (the stacking direction) and will give rise to diffuse streaks in single crystals, which in powder show up as characteristic asymmetric diffuse peaks [14].

For structural analysis of the SiC materials under study we choose the approach (ii) because it seems to be the easiest way to approximate the observed diffraction patterns: (i) would require tests with a very large number of very long period polytypes (and a very large number of atoms in unit cell which exceeds the capacity of standard Rietveld programs), while (iii) would require a special program to account for the characteristic line shapes [14] incorporated into a Rietveld program. On the other hand, (ii) only uses a few polytypes of medium period and can be tackled by a standard multiphase Rietveld program. Only the phase amount (scale factors) have to be refined! We used the version DBWS-9006 of the Rietveld program provided by R.A. Young. In the refinements some structural parameters (temperature factors, atomic positions) were kept fixed and the lattice constants were constrained to simplify multiples of the unit period c_0 . The polytypes used are summarized in Table II, together with corresponding %h.

Theoretical diffraction patterns calculated for models of twinned cubic structure of two domains of average size of 10–12 Si–C layers, e.g. (8 12), (9 13), (11 12) etc., are nearly identical and do not differ from the pattern calculated for untwinned 3C. In other words, the broadening resulting from twinning of 3C with the domains of the size 10–12 layers is too small comparing to the instrumental broadening (about 0.4 deg for neutron experiments) to be detected. This

TABLE II
Polytype structures of SiC used in the multiphase
analysis of α and β modifications of SiC.

Ramsdell symbol	Zhdanov sequence	Average twin stacking	Hexagonality %h
2H	1 1	1	100
4H	2 2	2	50
6H	3 3	3	33.3
10H	5 5	5	20
11H	5 6	5.5	18.2
13H	6 7	6.5	14.8
16H	8 8	8	12.5
15R	2 3	2.5	40
21R	3 4	3.5	28.6
24R	3 5	4	25
27R	4 5	4.5	22.2
3C	∞	∞	0

means that the lowest limit of detection of twinning by this technique and measured as hexagonality is not better than 10 %h. Clear indication of the presence of reflexion broadening due to stacking disorder is observed from 15 %h and very strong changes of the line profiles occur for 20–25 %h. One should note that the α - β classification of polycrystalline SiC materials based on diffraction techniques is not well substantiated by the content of hexagonal-like layers: there is a wide range of possible values of %h which are similar for α and for β , see Discussion.

5. Results

The experimental neutron diffraction patterns of SiC powders are compared in Figs. 2 and 3 to those calculated for multiphase models. Figures 2a and 3a present comparison to the patterns calculated for pure polytypes 3C and 6H, respectively. From this comparison it is clearly seen that the materials under study are not one-phase structures.

With the application of multiphase models the following results were obtained.

5.1. Sample I (β powder)

Figure 2b presents the neutron diffraction pattern (part of the pattern) which is compared to (a) calculated for pure cubic structure 3C and to (b) calculated for the multiphase model combined of 6 structures

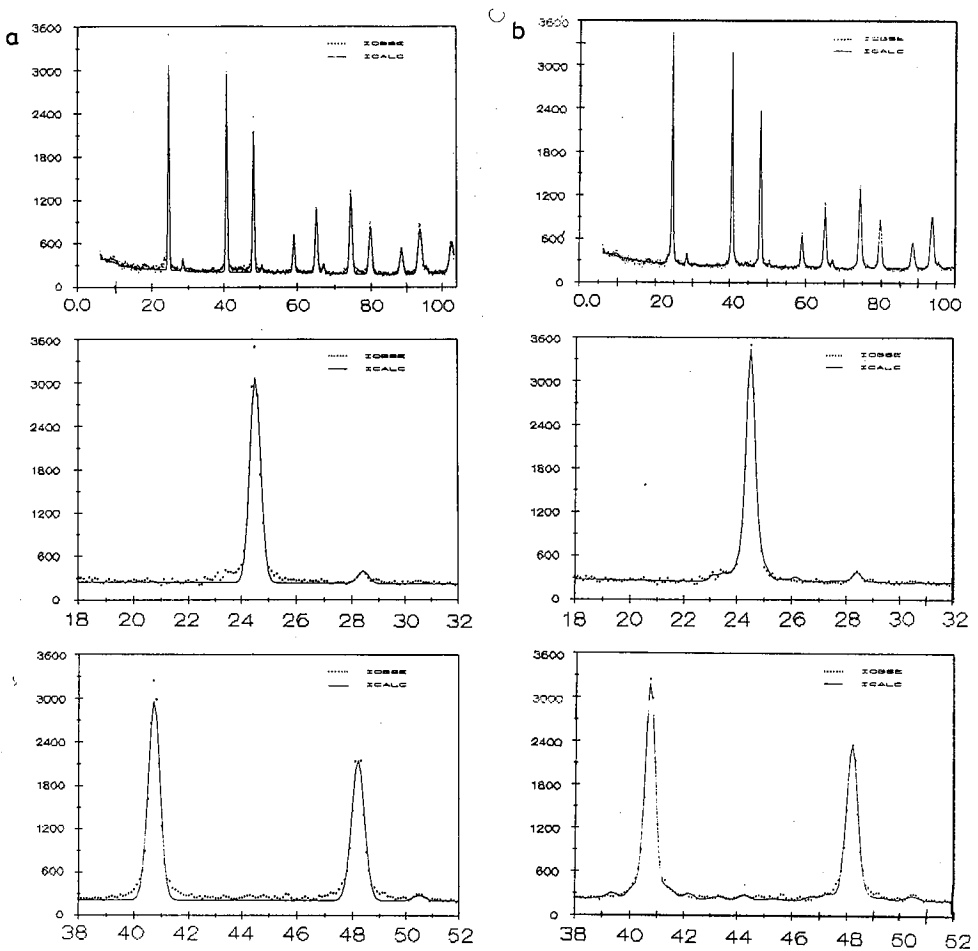
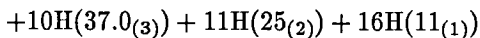
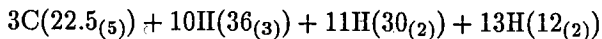


Fig. 2. Neutron diffraction patterns of sample I (β powder): (a) approximation of the experimental pattern by pure cubic 3C structure (one phase); (b) approximation of the experimental pattern by multiphase model: 3C + 4H + 6H + 10H + 11H + 16H.



(the values in brackets give the refined content of the polytypes in weight percent together with estimated standard deviations). The total hexagonality of the structure is 15.4 %h. The values R_{wp} and R_{exp} are 9.8 and 6.9, respectively.

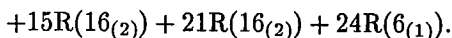
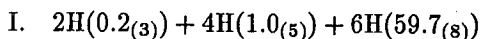
Similar agreements were obtained for models combined of other polytypes, e.g.:



where the total hexagonality is 14.4 %h and $R_{\text{wp}}/R_{\text{exp}} = 10.9/6.9$.

5.2. Sample II (α powder)

Figure 3 presents a comparison of the experimental data to the pattern calculated for pure polytype 6H (a) and for multiphase model combined of 6 polytypes (b). The model (a) of pure structure 6H was refined to $R_{wp}/R_{exp} = 12.2/4.3$. Several models were tried to approximate the disordered structure (b):



The total hexagonality of the structure is 33.5 %h, $R_{wp}/R_{exp} = 6.8/4.3$.

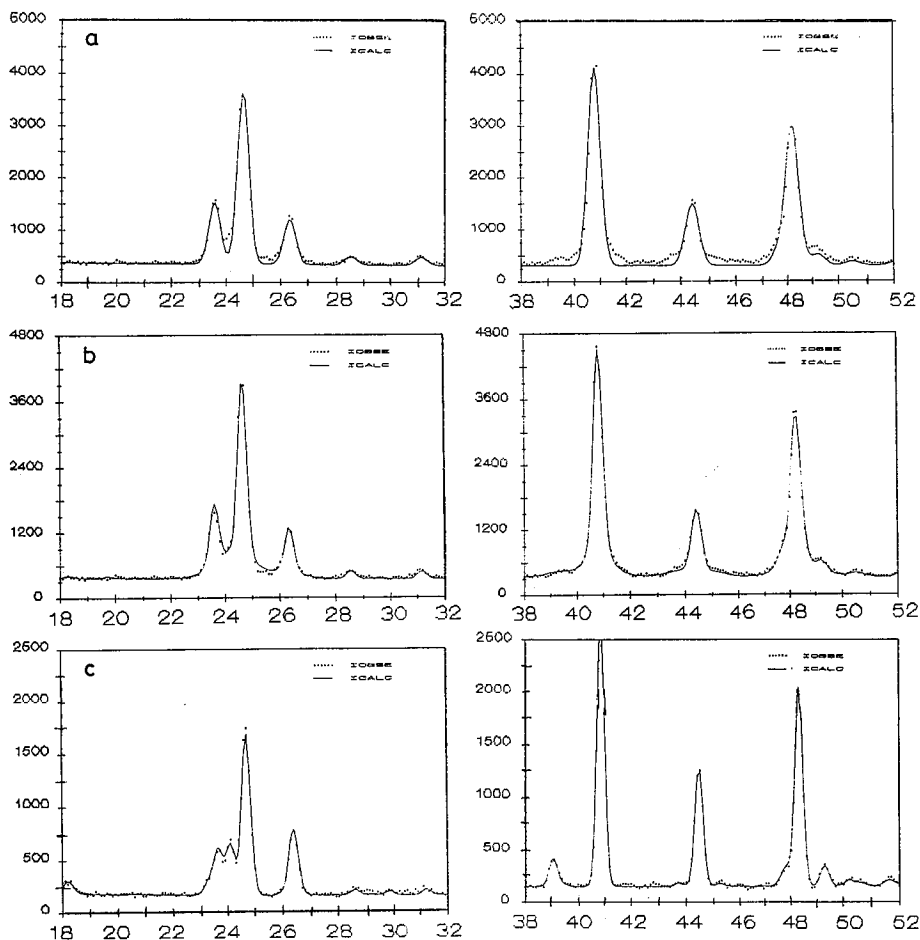
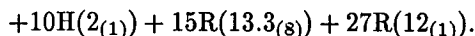
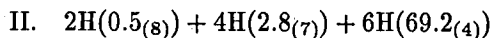


Fig. 3. Neutron diffraction patterns of α phases of SiC: (a) approximation of the experimental pattern of initial α powder, sample II, by pure 6H structure (one phase); (b) approximation of the powder pattern of sample II by multiphase model: 2H + 4H + 6H + 15R + 21R + 24R; (c) approximation of the experimental pattern of sintered α , sample III, by the multiphase model: 2H + 4H + 6H + 15R + 21R + 24R.

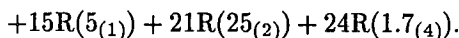
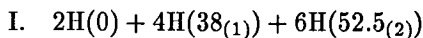
Similarly good fits of the patterns were also observed for other models, e.g. for the model where the structures 21R and 24R were replaced by 10H and 27R:



The resulting hexagonality of this model is 33.5 %h and $R_{\text{wp}}/R_{\text{exp}} = 7.9/4.3$.

5.3. Sample III (α sintered)

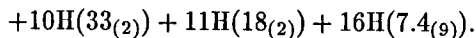
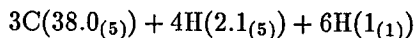
Figure 3c presents the neutron diffraction pattern of the α powder after sintering. The same multiphase models were calculated for the powder and for the sintered samples but only the model I gave a good fit of the patterns



The calculated content of 10H and 27R for the model II was very small: 0.8₍₈₎ and 1.2₍₉₎, respectively. The patterns were fitted very poorly, $R_{\text{wp}}/R_{\text{exp}} = 12.5/6.2$, which means that this model is inadequate for this particular structure. We note that in this structure having approximately 40 %h the average domain contains only 2.5 layers and it is not surprising that the phase analysis shows that there are very few domains 4 and 5 in the structure, cf. Table II — 10H and 27R.

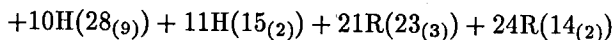
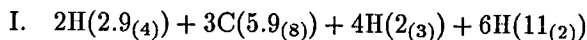
5.4. Samples IV, V

Figure 4 presents X-ray patterns of two different samples of β powder. The sample IV (Fig. 4a) is similar to sample I but with slightly smaller hexagonality

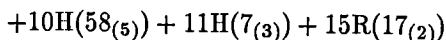
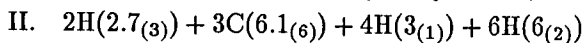


Total hexagonality is 12.1 %h, $R_{\text{wp}}/R_{\text{exp}} = 16.6/13.6$.

The pattern 4b of the sample V corresponds to another β powder which is significantly different from the samples I and IV. Several multipolytype models with different layer stackings were tried, e.g.



with total hexagonality 26.1 %h, $R_{\text{wp}}/R_{\text{exp}} = 20.5/16.4$,



with total hexagonality 28.3 %h, $R_{\text{wp}}/R_{\text{exp}} = 17/13.3$.

Note: Hexagonality 26–28 %h means that the average domain in this structure is about 3.7 layers. Despite the large hexagonality, one observes only the intensity maxima which can be attributed to the cubic structure 3C. A poor fit

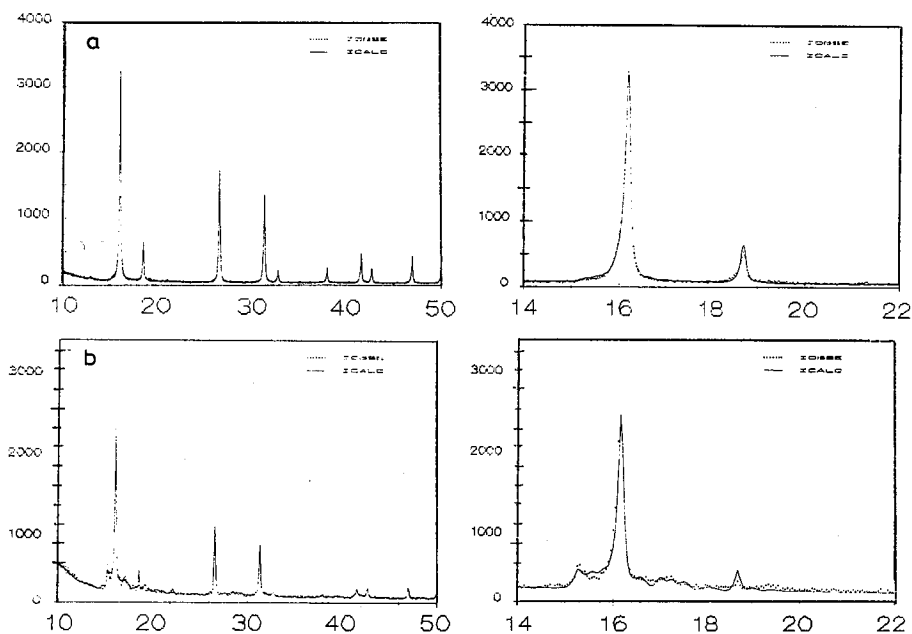


Fig. 4. X-ray diffraction pattern of β powders: (a) sample V, (b) sample VI by multiphase model: $2H + 3C + 4H + 6H + 10H + 16H$.

of the 3C reflexions suggests that either the sample is textured or the shape of the grains is strongly anisotropic. This sample shows very clearly how much the classification of the SiC powders into α and β can be misleading: the sample VI classified as β with about 27 %h is more α -like than cubic structure. At the same time the pattern of this structure exhibits no similarities to typical α patterns of Fig. 3.

6. Discussion

Figures 5 and 6 present distribution functions of the sizes of the domains of the 3C twins in α and β powders as derived from the phase analysis (relative content of different domains given as Zhdanov numbers). The multiphase model allows the calculation of only a few discrete points of the function for particular values of %h. In Fig. 5 the values derived from different models for the same powder sample are plotted together. These points fit well into one distribution function which proves that the derivation of the distribution function is independent from the chosen polytype composition.

Accepting the model of the polytype structures of the SiC β powders as resulting from the twinning of 3C, one accepts that there are no forces which could lead to periodic ordering. Under this assumption the twinning should be random. If this is true, the frequency of occurrence of domains of different sizes should be described by a statistical distribution function. In case of random disordering it

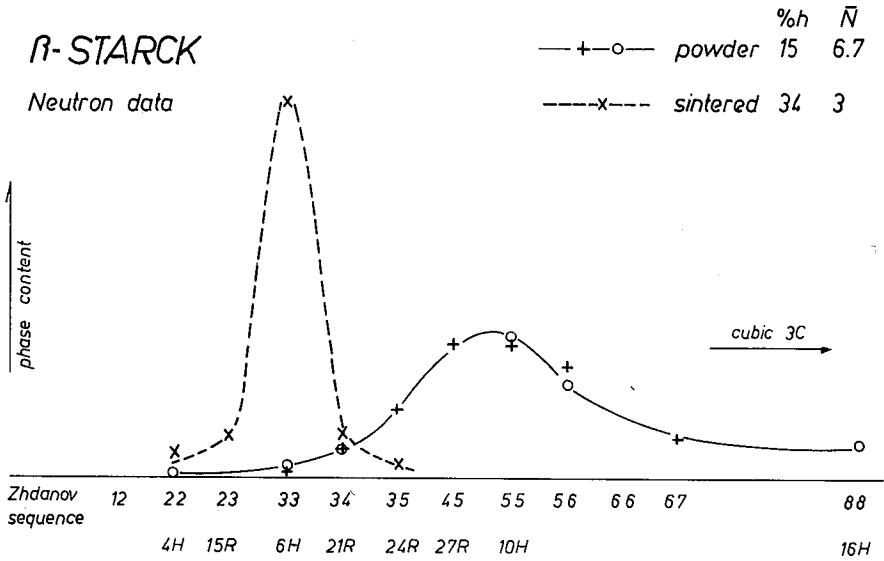


Fig. 5. Distribution of stacking sequences in the structure of the initial β powder (sample I) and in this powder after sintering (sample IV). Note: Two sets of the points calculated for two different models are plotted: + + + : $3C + 6H + 11H + 13H + 21R + 24R$, o o o : $3C + 4H + 6H + 10H + 11H + 21R$.

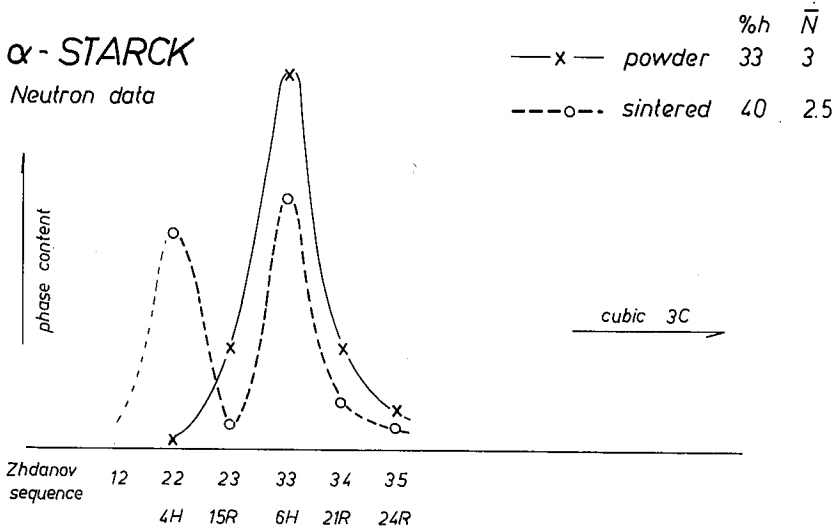


Fig. 6. Distribution of the stacking sequences in the structure of initial α powder (sample II) and this powder after sintering (sample III).

should be a *Gaussian*-type normal distribution function. The plots presented in Figs. 5 and 6 for α and β powders respectively are indeed similar to *normal* distribution function. However, the experimental function of β powder is not symmetric as one could expect. The parts of the curves corresponding to the larger domains are elongated which can be explained as due to the approximation of the twinned 3C structure with the domains larger than 8 by pure 3C.

Figure 5 compares the distribution functions of β powder before and after sintering. The hexagonality of the structure increases upon sintering from about 15 to 33.5 %h and the distribution functions of the initial and of the resulting structures are normal-type functions. The structural changes are then the transition of the initially randomly twinned structure 3C into another randomly disordered structure but with much smaller domains.

Figure 6 compares the distribution functions of α powder before and after sintering. The distribution function of the α powder is a symmetrical normal function as expected for the randomly disordered structure. The distribution function of the sintered material is split into two maxima corresponding to 4H and 6H stackings (22) and (33). This split can be explained by the following. In the initial α powder with 33.5 %h the average twin size is only 3 layers and the stacking sequence is given mainly by the domains 2, 3, 4 and 5. During sintering the individual domains divide into smaller ones. The development of the twinning, however, is possible only in the domains larger than 3: the domains 2 do not undergo further division into smaller domains because this domain (2 corresponds to hc stacking) is already the smallest single twin of 3C. The domains 3 also do not undergo further twinning because the division of this domain would require the creation of two domains: 1 and 2; of those the singular domain 1 does not occur, see above. The twinning occurs then only in the domains 4, 5 and larger and can develop only until the smallest domains are 2 and 3. The resulting structure of sintered α or β is very much enriched in the stackings 2 and 3 compared to the initial powders, which agrees very well with the distribution function of Fig. 6.

7. Final remarks and conclusions

In the present work we concentrated on the identification of the layer stackings in the α and β modifications of SiC powders and on the determination of the phase composition of the powders and of the sintered SiC. In general, a model of randomly disordered structure should include possibly large spectrum of the sizes of the domains which can have from 1 to an infinite number of the layers in a single domain. The calculations which we performed were limited to relatively simple models where the largest domain in the polytype cell was of 8 layers — 16H, Table II. Limitation of the maximum size of the domains in our models to 8 and approximation of other twinned structures by untwinned 3C may lead to a small underestimation of %h, e.g. up to 2.5 %h in β powder (sample I) and only 0.5 %h in sintered materials, e.g. sample II.

Performing the phase analysis we assumed that the lattice sites are fully occupied whatever the layer stacking is. There are indications, however, that in the structure of different polytypes there are certain deviations from stoichiometry

of SiC and, moreover, the polytype structure is strongly influenced by impurities, e.g. [10, 11].

The thermal parameters taken for the Rietveld analysis were fixed to $B_{\text{Si}} = 0.1$ and $B_{\text{C}} = 0.2$ and were not refined. The phase composition derived from the refinements with isotropic as above and with anisotropic parameters taken from single crystal data [13] were almost the same.

The results given here present a rather easy and quick way of characterizing polycrystalline (powdered or sintered) SiC samples. This work is now continued into direction of performance of quantitative phase analysis which will include the crystalline polytype phases and also non-crystalline phases present in polycrystalline SiC, in particular nanocrystals. For preliminary results see [15, 16].

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