

Modeling Studies of the Effect of Twins on the X-ray Diffraction Patterns of Boron Carbide

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Simulation studies were carried out to analyze the effect of planar defects (twins) on the X-ray diffraction patterns of boron carbide, B_4C . The presence of these defects had a marked influence on the patterns. Significant changes in the height, width, and other features of diffraction peaks are seen as a result of the presence of twins. The change in the patterns was directly related to the concentration of the twins. Two models were used for the location of the twin plane and the simulation showed a significant difference in the patterns for the same twin probability. The effect of grain size was also examined in this analysis. The results are compared with experimental observations on B_4C synthesized at different temperatures.

1. Introduction

Boron carbide is an important material in a variety of potential applications. These include its use as an abrasive material (because of its high hardness and high melting point), as a thermoelectric device material¹ (it is a wide gap p-type semiconductor with an anomalously large Seebeck coefficient), and in control rods for nuclear power generation.² As in other boron-rich phases,³ the structure of boron carbide is based on boron-rich icosahedra which are bonded by carbon and boron atoms. Boron carbide is nominally assigned the formula B_4C , although it has a wide range of homogeneity, ranging from B_4C to $B_{10.5}C$ and corresponding to a composition range of about 20 to 9 at. %C, respectively.² This relatively large range of composition leads to the presence of point defects and crystallographic disorder.² Such defects play an important role in its electrical and thermal behavior.⁴

The role of defects in the interpretation of X-ray diffraction patterns was demonstrated by the results of a recent study.⁵ The grain size of fine-grained B_4C synthesized (at relatively low temperatures, <1500 °C) and densified simultaneously was evaluated from X-ray line-broadening analysis using the Halder–Wagner method. The crystallite size was nanometric, being in the range 20–40 nm. However, transmission electron microscopy (TEM) observations showed a wide range of grain size extending from >100 nm to several micrometers. The

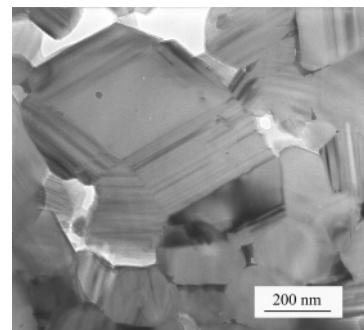


Figure 1. TEM micrograph showing twins in B_4C (modified from ref 5).

large discrepancy between the two sets of grain size results was attributed to the presence of high concentrations of twins in the boron carbide. Domains in a grain that possesses twins confined to a single set of planes give diffraction that is equivalent to crystallite the size of the these domains. The presence of such a high level of crystallographic disorder in B_4C was never been reported before, and no quantitative interpretation of its influence on the X-ray powder pattern has been investigated. The presence of twins in a B_4C sample synthesized in the referenced work is exemplified by Figure 1.

In this paper we present results of an investigation on the effect of twins on the XRD patterns of B_4C . The modeling study is based on the diffraction theory of one-dimensionally disordered crystals, examining the structural changes in boron carbide based on the occurrence of plane defects. The importance of these one-dimensional defects in the sintering of SiC has recently been investigated.⁶ In that case, the prevalent defects are stacking faults.

2. Modeling Studies

A. Background. As was observed in a recent study⁵ and as has been reported by others,^{7,8} boron carbide typically contains a high concentration of twins. Their

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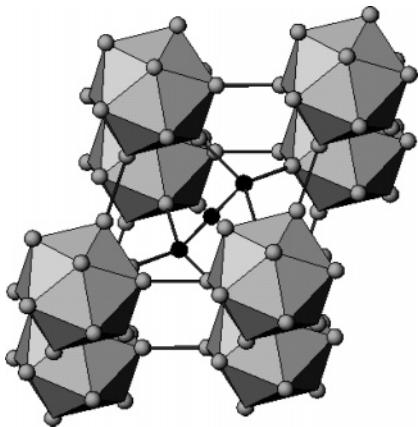


Figure 2. Structure of boron carbide.

presence has been verified by high-resolution transmission electron microscopy, HRTEM,^{7–9} although their occurrence can sometimes be ascertained even with lower resolution microscopy.^{10–13} The presence of twins can significantly alter the characteristics of the XRD patterns¹⁴ by introducing peak shifts, peak broadening, and in some cases, by the disappearance of peaks or the appearance of others.

The nature of twins in boron carbide can be ascertained by examining the simplest model of crystallographic structure for the composition B₄C. Although the general features of this structure have been established for sometime,¹⁵ many details have yet to garner full agreement.^{16–21} The structure of B₄C can be described using either a rhombohedral or a hexagonal unit cell. Using rhombohedral axes the cell contains 15 atoms, corresponding to B₁₂C₃. The structure is represented by 12-atom icosahedral units centered on the corners of the rhombohedral cell and a three-atom chain located along the 3-fold (diagonal) axis at the center of the cell, as shown in Figure 2. Both atoms at the end of the chain are bonded covalently with the closest atom of three icosahedra. Each icosahedron is connected to

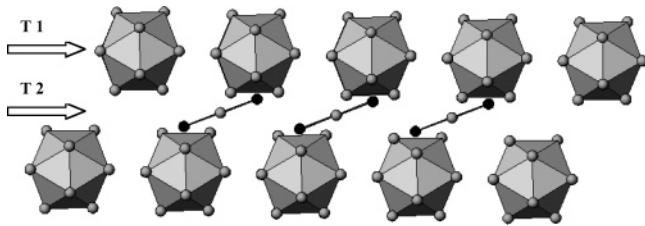


Figure 3. Projection of the crystallographic structure of B₄C parallel to the basal plane.

six others through covalent bonds. The structure is closely related to that of α -boron, which does not include the chain of atoms along the 3-fold (diagonal) axis. Most of the controversy regarding the structure centers on how the experimentally observed large change in stoichiometry can be reconciled with the structure. It had been reported from X-ray and NMR studies that the structure is made up of B₁₂ icosahedra joined by C–C–C chains.^{22,23} Other models and experimental results suggest the existence of B₁₁C icosahedra joined by C–B–C chains.^{24–26} When the C content decreases, the B₁₁C icosahedra are initially retained, while one of the carbons in the chain C–B–C is gradually replaced by boron, i.e., forming C–B–B chains. Only at the compositions richest in B (at about 13 at. % C) does the C content of the icosahedra begin to decrease. This model, proposed originally by Emin,¹⁷ has seen several modifications, including the presence of ionic B and of vacancies.²¹

The crystallographic structure of B₄C can be viewed as layers of icosahedra, as shown in Figure 3, where a projection of the structure in the direction parallel to the basal plane (001) is depicted. On the basis of TEM observations, Mackinnon et al.⁷ proposed that twins lie only in this plane. This, however, does not unequivocally identify the nature of the twin since that would require defining its position in the direction perpendicular to the plane. In a subsequent study, Miller and Mackinnon⁸ proposed two possible positions for the twin plane, identified as T1 and T2 in Figure 3. From image simulation on HRTEM data, these authors concluded that the twin plane passes through the center of the icosahedron (i.e., T1 in Figure 3), distorting the inter- and intra-icosahedron bonding. The alternative position, T2, is through the center of the three-atom chain, as shown in Figure 3. Mackinnon et al.⁷ observed a high degree of faulting in typical sintered samples with a typical twin dimension of about 2.5 nm reported for samples sintered at 2100 °C.

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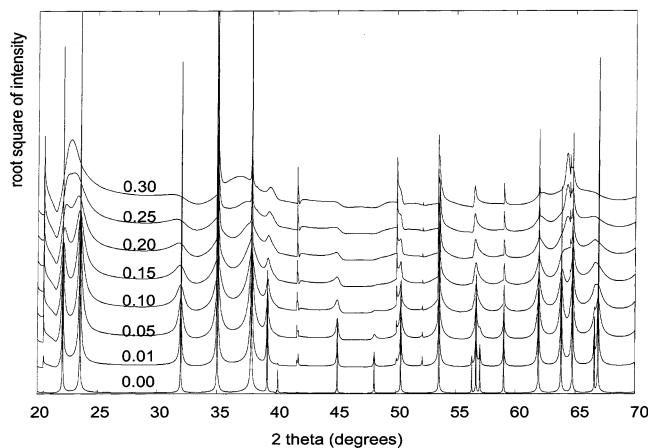


Figure 4. Results of simulations depicting the dependence of the XRD pattern of B_4C on the probability of twin occurrence, α .

B. Simulation Studies. To identify the influence a high degree of faulting can produce on the XRD patterns of B_4C , we performed computer simulation using the program DIFFaX.²⁷ This program makes possible the simulation of the diffraction pattern of any structure containing planar faults (such as twins and stacking faults) and the evaluation of the incoherent intensity distribution due to faults with a random distribution. Since the program does not accept structures with a γ angle different from 90°, a new elementary cell that lies on the (001) plane of the original rhombohedral structure and containing 30 atoms has been used to describe the structure. In the simulation we define α as the stacking probability. It is the probability that a given layer will be followed by a layer with the wrong stacking sequence. The diffraction intensities are then calculated for a statistical ensemble of crystallites, each with a distinct stacking sequence, but weighted by the probability that such sequence will occur. The program also can take into account the effect of crystallite sizes. The directions **a** and **b** lying on the twin plane are treated considering a Scherrer-type peak broadening due to a finite layer width. Small crystallite sizes in the direction perpendicular to the twin plane can be specified indicating the number of layers that must be included in each crystallite.

The results of the simulations are depicted in Figures 4 and 5 as XRD patterns for B_4C with different concentrations of twins (different values of α). In both figures the diffraction intensity is plotted as the square root to give more emphasis to the low intensity features. In Figure 4 the peaks from coherent diffraction are seen as very sharp vertical lines (with no width), making the diffuse scattering from the stacking defects more discernible. It is clear from this figure that the density of twins markedly affects the features of the diffraction pattern for B_4C . As the density increases, regions of diffuse scattering appear around several peaks, altering their shape and modifying their width. Broad halos appear at 2θ values of about 23° and 37°, while an extended asymmetric tail appears in the region at high end of the peak at 23°. Other peaks, such as those at 32, 39, 45, and 67°, became so broad that they practi-

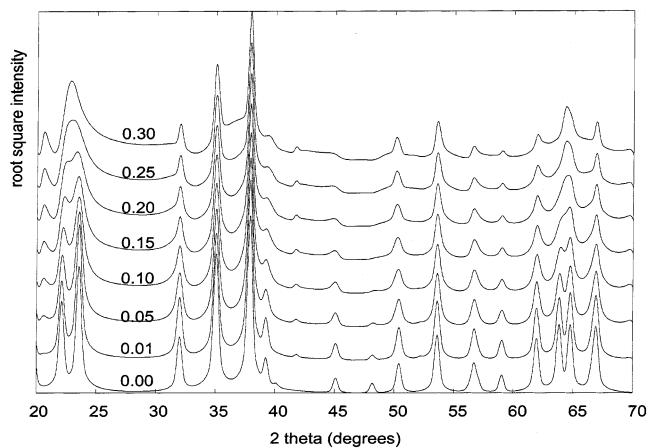


Figure 5. Results of simulations depicting the dependence of the XRD pattern of B_4C on the probability of twin occurrence, α . The instrumental peak widths have been represented using a Voigt function with the parameters $u = 0.05$, $v = -0.036$, $w = 0.15$.

cally vanished. Even more interesting is the merging of the doublets at 23° and 64°. A more realistic picture of the changes these modifications introduce in a powder pattern can be seen in Figure 5. In this figure a reasonable line width was used for the coherent diffraction components of the peaks, approximating instrumentally generated line widths.

3. Discussion

The alteration of X-ray diffraction patterns by the presence of stacking faults in another carbide, β -SiC, has been investigated experimentally and by simulation.^{28–30} The results showed that the presence of stacking faults and twins lead to changes in the diffraction peaks, as was seen in this study for B_4C . As was pointed out in our previous study,⁵ such changes can lead to misinterpretation of the results when diffraction patterns are used for crystallite size evaluations. As can be seen from Figure 5, the presence of planar defects results in a decrease in line intensity, an increase in the width of the peaks, and an increase in the background intensity. The magnitude of these changes depends on the density of defects in B_4C . Similar observations were made for the case of SiC.²⁹

Significant diffuse diffraction is observed in simulations with relatively low stacking probability, $\alpha > 0.1$. For $\alpha = 0.1$, the structure is such that there is a 10% probability of having a wrong plane sequence, or an average of one twin every 10 layers. Since each layer is 0.44936 nm thick, an average twin thickness of about 4 nm is calculated. In a previous study,⁵ we reported the smallest twin thickness as 5 nm in B_4C . Mackinnon et al. reported a typical twin dimension of about 2.5 nm for samples sintered at a high temperature (2100 °C).⁷ In a recent study³¹ we have shown that at such a high temperature, no indication of the presence of twins can be obtained from the X-ray pattern. On the other hand, samples sintered at much lower temperatures are expected to contain twin densities that are much higher;

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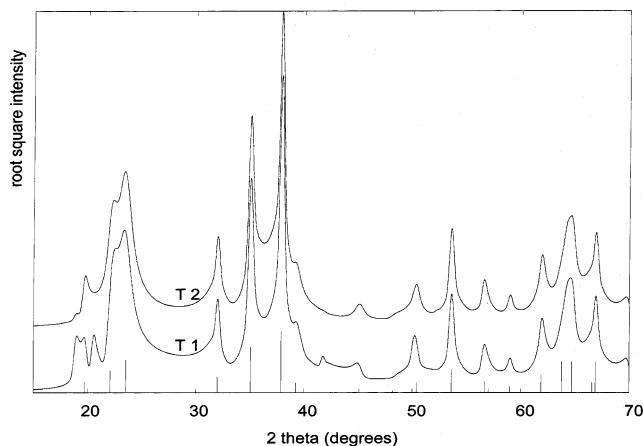


Figure 6. Simulated XRD patterns for B_4C with two locations of the twins (T1 and T2 in Figure 1); $\alpha = 0.20$.

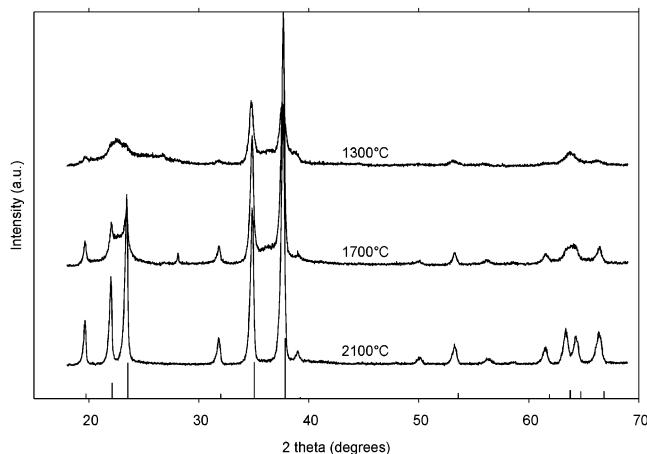


Figure 7. XRD patterns of B_4C synthesized at low, intermediate, and high temperatures (modified from ref 31).

thus a stacking probability of 0.2–0.3 would not be unreasonable.

The simulations presented thus far have assumed the twin model proposed by Miller and Mackinnon,⁸ i.e., the twin plane runs across the center of the icosahedra (T1 in Figure 3). To show the effect of using the alternative twin model, we carried out simulations assuming T2 as the location of the twins for a constant α . The results are shown in Figure 6 as a comparison between the two twin models (T1 and T2) for $\alpha = 0.20$. The patterns from both models are generally similar, except for the region at low angles, around $2\theta = 20^\circ$. Here the T1 model (with the twin planes running across the centers of the icosahedra) shows the presence of two extra peaks which are not observed in the pattern for the T2 model, or in the pattern for the fault-free B_4C . The latter is represented by the lines on the bottom of the graph. These extra peaks are the result of the distortion in the bonding within the icosahedron introduced when the T1 model is used.

The changes in the XRD patterns obtained in this study are generally in good agreement with those obtained experimentally.³¹ Figure 7 shows the XRD patterns of B_4C for three synthesis temperatures: low, intermediate, and high. The synthesis was accomplished by reacting elemental boron and carbon in a spark plasma synthesis (SPS) apparatus, as described in a recent paper.⁵ Comparing the patterns obtained by

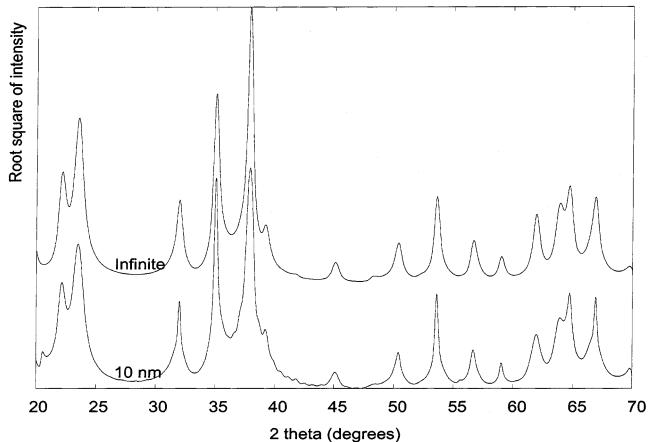


Figure 8. Simulated XRD patterns for B_4C with two different crystallite sizes in the direction perpendicular to the twin plane; $\alpha = 0.20$.

modeling (Figure 5) with those obtained experimentally (Figure 7) shows that changes in synthesis temperature correlate with changes in the density of defects. At low and intermediate temperatures (1300 and 1700 °C) the experimental patterns are similar to those with relatively high twin concentration (α : 0.2–0.3). In both cases broad halos at 2θ values of about 23° and 37° are evident. Also, the peaks at 32 , 39 , and 67° are broad and have low intensities and the doublets at 23° and 64° are merged. As the synthesis temperature increases, the experimental patterns become similar to those modeled with low twin density. The pattern obtained at 2100 °C is very similar to that obtained with zero or very low concentration of twins ($\alpha = 0.01$).

Another aspect related to the experimental XRD results concerns the relative intensities of the two main peaks (at 2θ values of about 38 and 35°) and their change with temperature. Examination of Figure 7 reveals that the samples annealed at 1300 °C show intensities of these two peaks that are nearly equal, while in the pattern of samples annealed at 2100 °C and in the modeling study (Figure 5) the peak of the higher angle is significantly larger. Twins can produce a significant change in peak width and a decrease in intensity, but no change in the relative intensities of the peaks is expected. The simulation, however, shows that the relative peak heights are dependent on particle size. Simulations were made with a constant twin probability ($\alpha = 0.10$) but with two different particle sizes (infinite and 10 nm) in the direction perpendicular to the plane of the twins. The results, presented in Figure 8, show that for samples with large grains (here assumed infinitely large) the peak at 2θ of about 38° has a much higher intensity than the peak at about 35° . When the grain size is assumed to be small (10 nm), the heights of these two peaks become comparable. In the recent referenced study on B_4C ⁵ it was shown that samples contained both large (a few micrometers) and small (nanometric) particles. Thus, a complete interpretation of the experimental XRD results must include the role of possible size inhomogeneity. The change of the relative heights of the two peaks ($2\theta = 35$ and 38°) with temperature indicates the presence of small particles at low temperatures and the increase in their size with increasing temperature. These conclusions are consistent with TEM observations.³¹

4. Summary and Conclusions

In a previous study on B₄C, the marked discrepancy between crystallite sizes obtained from TEM observations and from X-ray line broadening analysis was attributed to the presence of a high density of twins.⁵ In this study, the effect of these planar defects on the XRD pattern of B₄C was investigated by simulation using the program DIFFaX.²⁷ The results show that the presence of twins has a significant effect on the pattern, with the degree of pattern alteration being a function of the density of the twins. Two locations for the twin planes were considered and the results show pattern

dissimilarities dependent on the assumed model. The simulation also showed that grain size plays a role in modifying the XRD patterns of B₄C. The results of the modeling study are in agreement with experimental observations.

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