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Polytypism of SiC and interfacial structure in SiCp/Al composites

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In the present work, the polytypism of SiC and the interfacial structure between SiC and Al were investigated using X-ray diffraction (XRD) and high resolution transmission electron microscopy (HREM). It was approved that 15R could be juxtaposed with 6H stacking sequences in the same SiC reinforcement and a structural transformation zone was also observed. The Al_4C_3 compound can nucleate on SiC at the SiC/Al interface with the growth orientation parallel to the *C* axis of SiC. Mechanisms for the observed phenomena were also discussed in detail. © *2002 Kluwer Academic Publishers*

1. Introduction

Metal/ceramic interfaces are currently receiving a great deal of interest in metal matrix composites (MMCs) since these regions control the efficiency of load transfer from matrix to reinforcement. The strength of the composite material without interfacial bonding is doubtful regardless of how strong or stiff the matrix and the reinforcement. Interfacial structures in SiC/Al composite system have been widely studied. Several different models have been proposed to describe the types of bonding at the interfaces between SiC and Al [1–4]. Basing on these investigations, a sufficient strong isotropic bonding could take place through chemical reactions between the matrix and reinforcement forming an oxide layer along the interface, diffusion of atoms, or an atomic interaction at the interface causing a bond without the formation of distinct reaction products. However a strong chemical interaction will cause degradation of the reinforcement increasing the possibility of undesirable phase such as Al_4C_3 in SiC/Al composites [5–8].

Even though it is of interest, the interfacial structure between SiC and Al in composites is not fully understood because of its complexity and dependence on many variables. Most of the works were concentrated on the effects of production methods of composite such as squeeze casting, hot-pressing of layers, second phase at the interface, and the specific orientation relationships between SiC and Al [9–13]. Unfortunately, polytypism of SiC reinforcement upon the interfacial structure was less reported, although it is quite necessary to get insight into the nature of the reinforcement/matrix interface. Since the long-term structure of silicon carbide is extremely complex as a result of the one-dimensional disorder or polytypism, it is inevitable that the polytypism of silicon carbide play an important role upon the interfacial structure between SiC and Al in composites.

Accordingly, in the present work, the polytypism of silicon carbide and its effect upon the interfacial structure in SiCp/Al composite were investigated using X-ray diffraction (XRD) and high resolution transmission electron microscopy (HREM).

2. Experimental

2.1. Material preparation

SiCp/pure Al composites used in the present study were fabricated using vacuum-high pressure infiltration processing, the temperature of the SiC reinforcement preform $t_p (t_p = 650°C)$ and that of the pure Al melt $t_m (t_m = 750°C)$ were controlled separately. After infiltration, the composite material cooled with the furnace. In the composite material, the average particle size of dominant SiCp phase was about 7 μm. SiCp used in this study had not undergone any surface modification such as surface oxidation, surface coating etc.

2.2. X-Ray diffraction

The as-received SiC powders were firstly characterized by X-ray diffraction. A JEOL, JDX-3530M diffractometer using Ni filtered Cu K_α radiation at 20 KV and 20 mA was employed to obtain a chart recording in the 2θ range from 20° to 90° with a scanning step of 0.2°/Sec.

2.3. HREM observation

The structural characteristics of the SiC reinforcement and of the SiCp/Al composites interface were

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further investigated using a Hitachi-9000 high resolution transmission electron microscopy (HREM) operated at 300 KV. HREM samples were prepared by cutting 0.7 mm slices with a low-speed saw which were then mechanically polished to a thickness of 200 μm. Finally, 3 mm diameter discs punched from these slices were dimpled and ion milled with argon at an angle between 10° and 20° with 6 KV and 2 mA.

3. Results

Fig. 1 shows the X-ray diffraction profile for the SiC particles used in the present work. This pattern shows that the main polytype in the samples is of hexagonal structure denoted mainly 6H. From a comparison between the calculated 6H spectrum and the experimental one observed, it is shown that besides 6H SiC polytype, one or several other SiC polytypes, for example, 15R-SiC are also present.

Unfortunately, it is still not clear how 6H and 15R sequences exist and arrange in the SiC particles, and it is not straightforward to identify these by x-ray diffraction, so HREM technique is further employed.

All silicon carbide structures are made up of a single basic unit, a plane tetrahedral, arbitrarily either SiC4 or CSi4. Successive layers can arrange themselves in one of the two ways: parallel or anti-parallel, respectively. Arbitrarily designating one orientation "a", the other "b", the parallel stacking of layers leads to an "aa" sequence while the anti-parallel yields a "bb" sequence. The common structures, those of 6H and 15R-SiC, have "aaabbb" and "aaabb" layer sequences, respectively. Each of these structures can be considered as having planes of carbon atoms (or of silicon atoms), viewed either as packed ions or as centers of tetrahedral stacked one above another in different arrays. For 6H-SiC and 15R-SiC, Fig. 2 shows the schematic illustration of these two crystal structures on (1120) plane.

Figs 3 and 4 shows the HREM images of 6H SiC and 15R SiC on (11$\bar{2}$0) plane respectively. As seen in the figures, the ideal structures for 6H-SiC and 15R-SiC, have "ABCACBA" or (3,3) sequence, and "ABCACBCABACABCA" or $(3,2)_3$ sequence, respectively. On the other hand, as in most cases, the juxtaposition of 6H and 15R stacking sequences in the same SiC reinforcement were also frequently observed in the present work. Fig. 5 shows a typical example of polytype sequence of this case in the same silicon carbide particle. From the selected area diffraction (SAD) pattern, it can be found that this SiC phase is not either ideal 6H or ideal 15R SiC. While from the HREM image, it is notable that both 6H or (3,3) sequence and 15R or $(3,2)_3$ sequence are present in the same SiC particle reinforcement. Furthermore, structural transformation zone between (3,3) sequences and $(3,2)_3$ sequences, marked as D, is also clearly observed in Fig. 5.

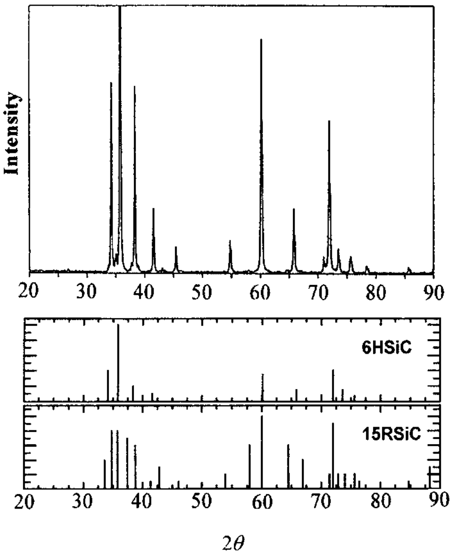

Figure 1 X-Ray diffraction profiles for the SiC particles used in present work.

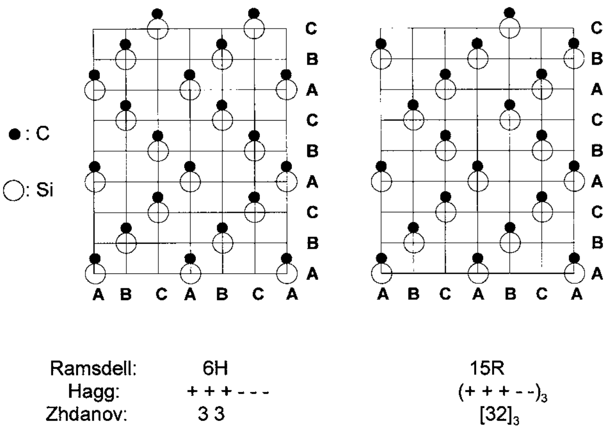

Figure 2 Schematic illustration of SiC structure on (11$\bar{2}$0) plane, (a) 6H-SiC (b) 15R-SiC. Where Hagg: +: parallel, A → B → C → A, -: anti-parallel, A ← B ← C ← A; Ramsdell: stacking number in one + crystal structure; Zhadanov: Number of +, Number of −, Number of +, . . .

An interesting interfacial structure in SiCp/Al composite derived from the 6H and 15R polytypism was also observed in the present work. Fig. 6 shows a typical example where Al_4C_3 nucleates at specific sites on the SiC substrate particle with 6H and 15R polytypism. Fig. 7 shows the enlarged image of partial zone of SiC particle, marked as G in Fig. 6. As seen in Fig. 7, the bold lines are 15R sequences and the thin lines are 6H sequences, thus both 6H and 15R stacking sequences occurs in this particle. The situation illustrated in Fig. 6 refers to the case of a coherent precipitate of Al_4C_3 in the SiC particle. The lattice parameters of Al_4C_3 are different from those of the SiC particle, as seen in Table I, and a stress-strain field is set up in the SiC particle and Al_4C_3 precipitated, which give rise to the diffraction contrast. The result suggests that aluminum penetrating the SiC grains is already carbon-saturated and, consequently, Al_4C_3 crystals grow in the particles wherever a temporary local supersaturation is produced. This typical image suggests that Al_4C_3 can nucleate on the base level of SiC with a growth orientation parallel to the C axis of SiC. This result agrees with that of Yano *et al.* [14].

TABLE I Structure parameters of SiC and Al_4C_3

Crystal	Structure	Space group	*a* (nm)	*c* (nm)
SiC	6H	P63mc	3.073	15.08
SiC	15R	R3m	3.073	37.70
Al_4C_3	Rhombohedral	Rd3m	3.329	24.98

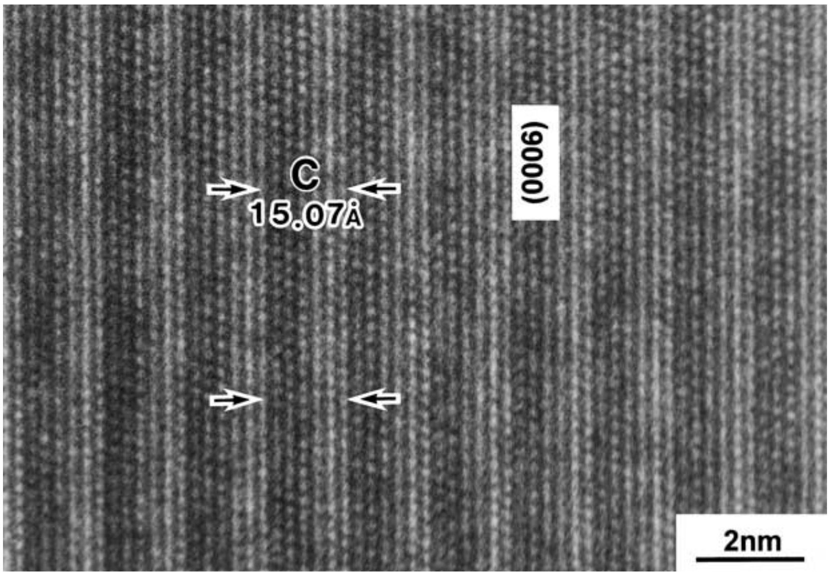

Figure 3 HREM image of 6H-SiC on $(11\bar{2}0)$ plane.

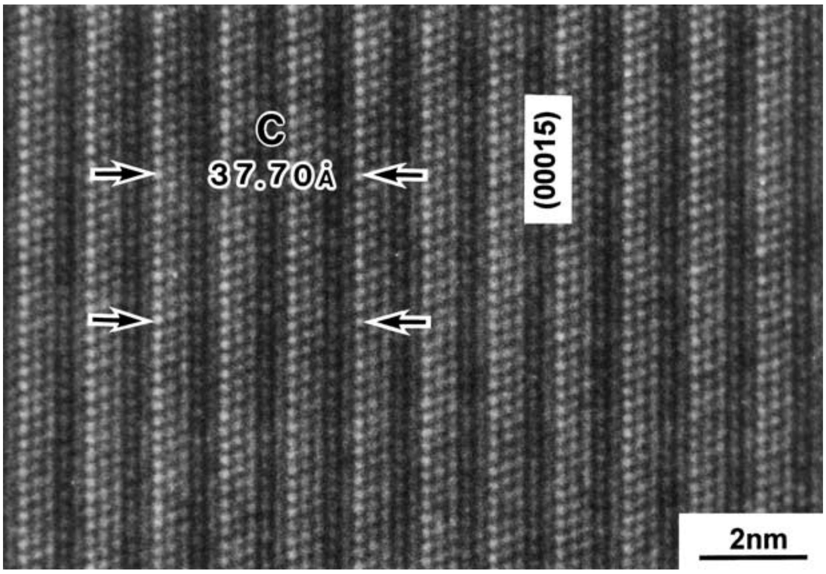

Figure 4 HREM image of 15-RSiC on $(11\bar{2}0)$ plane.

4. Discussions

4.1. Juxtaposition of 6H and 15R sequence

As indicated above, the phenomenon in which 15R could be juxtaposed with 6H stacking sequences in the same SiC reinforcement was observed. On the basis of screw dislocation mechanism, Mitchell *et al.* [15–21] explained the SiC structures in detail, but here, it is still interesting enough for the transformation between 6H-SiC and 15R-SiC, and the structural transformation between the two polytypes could be further explained as follows.

Fig. 8 shows the matching view of 6H-SiC and 15R-SiC on $(11\bar{2}0)$ plane in one period of 15R-SiC. The structure of SiC viewed parallel to the hexagonal axis consists of hexagonal double layers, each layer consisting of single atomic species and the alternate atoms located directly above one another. Since the bonding of both atoms in SiC is tetrahedral, additional double layers could attach themselves in only two positions. Among these three orientations, the only ones possible could be designed as A, B, C. Considering the structure of SiC on two layer arrangements of a, b and stacking orientation of successive tetrahedral layers, the layers of tetrahedral could be arranged in space in three non-identical position A, B and C. If they could be arranged at the order of "ABCACBA" or (3,3) sequence, the structure would be 6H-SiC, as the stacking sequence of "○" illustrated in Fig. 8. But it would in reality not be stable since the layers would all have the same spatial position AAA. . ., BBB. . . or CCC. . ., etc. Since two adjacent layers in the case of tetrahedral bonding could not have the same position AAA. . ., BBB. . . or CCC. . . etc., each successive layer must undergo a translation parallel to the plane of the growth surface. The translation would occur in the same direction every time, the stack moves through one pitch, and horizontal displacement is necessary to maintain continuity in the Si-C zigzag "chain", thus it could come back to an identical situation. Three shifts in the same direction would bring the stack back into its original position, completing one repeat period. It is easy to see that the resulting structure would have a rhombohedral lattice. If they could be

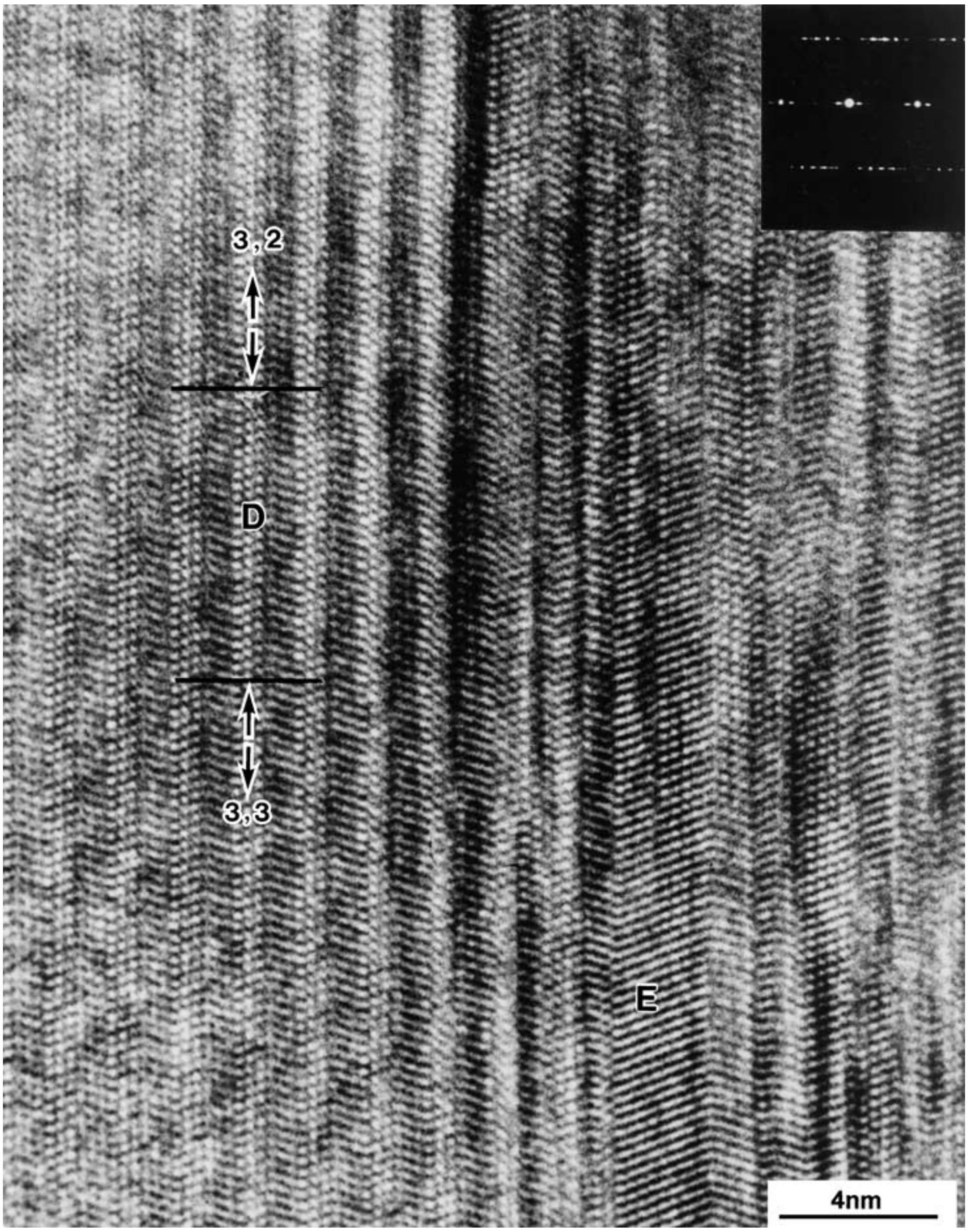

Figure 5 HREM observation of SiC on $(11\bar{2}0)$ showing polytypism in the same SiC reinforcement and transition zone between 6H and 15R stacking sequences.

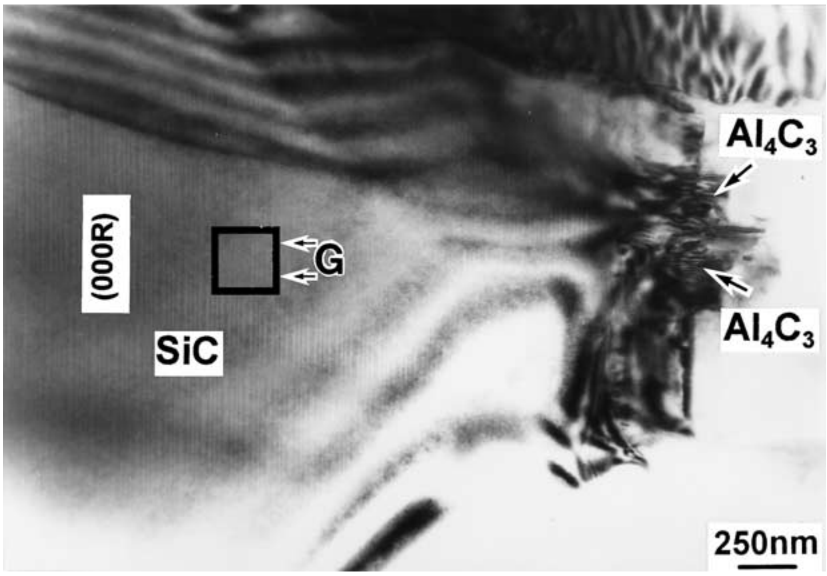

Figure 6 HREM image of SiC/Al interface, showing nucleation of Al_4C_3 on SiC subtract.

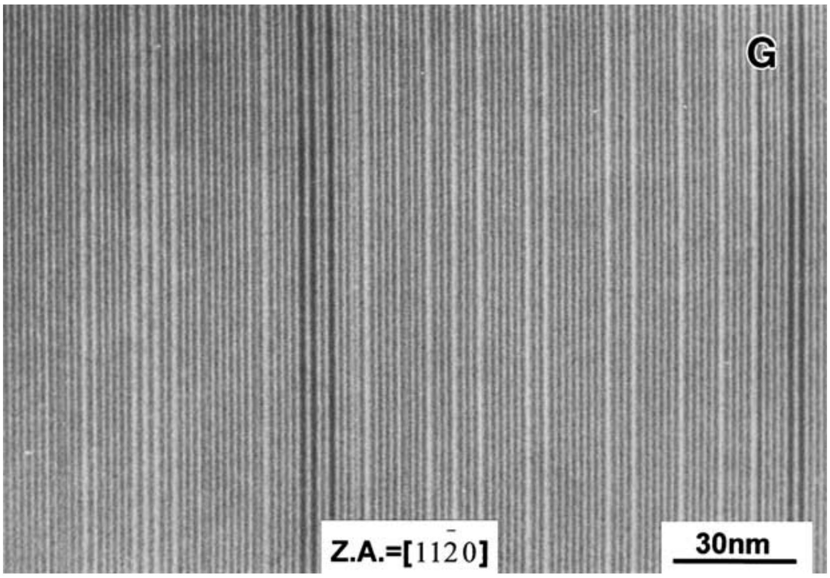

Figure 7 Enlarged image of partial SiC marked as G in Fig. 6.

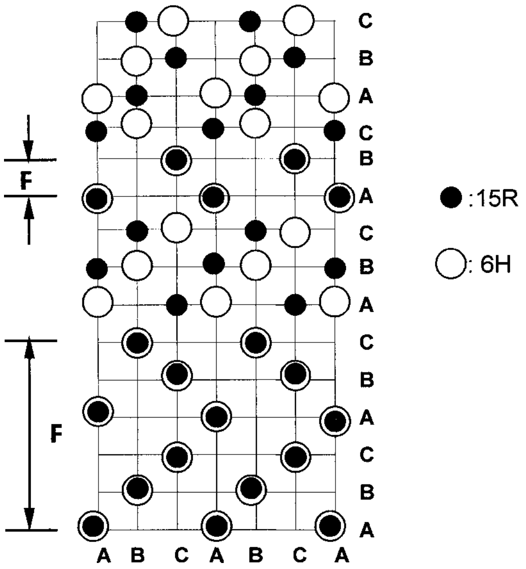

Figure 8 Matching view of 6H-SiC and 15R-SiC on (11$\bar{2}$0) plane in one period of 15R-SiC.

arranged at the order of "ABCACBCABACABCBA" or $(3,2)_3$ sequence, it would be 15R-SiC, as the stacking sequence of "•" illustrated in Fig. 8.

Furthermore, during the stacking period of 6H or 15R-SiC, its stacking basic unit may have the same positions after a certain stacking along the C axis, as marked as F in Fig. 8. In these cases, two further stacking sequences would be possible: either arranged at the order of 6H, or arranged at the order of 15R. From this atomic matching figure, it is easy to be found that 15R could be juxtaposed with 6H stacking sequences in the same SiC reinforcement and there would be a structural transformation zone between the two during their stacking growths.

4.2. Nucleation of Al_4C_3 on SiC reinforcement with 6H and 15R polytypism

In the HREM observation of the present work, it was shown that Al_4C_3 could nucleate on SiC base level, and the growth orientation parallels to C axis of SiC, which is associated with the structure parameters of 6H-SiC and 15R-SiC crystal as follows:

6H-SiC

Space group: C6mc

Atomic Position: Si at 000, 0 $0\frac{1}{2}$, $\frac{1}{3}\frac{2}{3}\frac{1}{6}$, $\frac{1}{3}\frac{2}{3}\frac{5}{6}$, $\frac{2}{3}\frac{1}{3}\frac{2}{3}$, $\frac{2}{3}\frac{1}{3}\frac{1}{3}$

C at 0 $0\frac{1}{8}$ plus each Si position

Unit Cell: $a_0 = 3.073$ Å, $C_0 = 15.079$ Å

15R-SiC

Space Group: R3m

Atomic Position: Hexagonal System

Si at 0 0μ, $\frac{1}{3}\frac{2}{3}\frac{1}{3}+\mu$, $\frac{2}{3}\frac{1}{3}\frac{2}{3}+\mu$, $\mu = 0, \frac{2}{15}, \frac{6}{15}, \frac{9}{15}, \frac{13}{15}$

C at 0 $0\frac{1}{20}$ plus each Si position

Unit Cell: $a_0 = 3.073$ Å, $C_0 = 37.70$ Å

As seen above, it is worth noting that 6H-SiC and 15R-SiC have the same lattice parameter on base level, i.e., $a_0 = 3.073$ Å, and have the same step height along C axis, i.e., $(\frac{15.079}{6} = \frac{37.70}{15})$. 6H-SiC and 15R-SiC are made up of the same basic unit, either SiC_4 or CSi_4, the only difference lies in that they have different stacking sequences along the C axis. From these, it can be further deduced that the nucleation and growth of Al_4C_3 would be associated with the stacking orientation along C axis, and have nothing to do with the polytypism in SiC.

5. Conclusion

The polytypism of SiC and the interfacial structure between SiC and Al were investigated using X-ray diffraction and high resolution transmission electron microscopy. The results indicates that 15R could be juxtaposed with 6H stacking sequences in the same SiC reinforcement, thus there must be a structural transformation zone between the two sacking sequences. The present work provides the clear evidence that Al_4C_3 compound can nucleate on SiC substrate at the SiC/Al interface with the growth orientation parallel to the C axis of SiC. The observed phenomena are due to the specific characteristics of stacking sequences along the C axis in 6H and 15R-SiC.

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