Crystallinity of SiC Coated on Carbon Fiber

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The structure, crystallinity and preferred orientation of the SiC coated on carbon fiber at 1200°C from mixtures of monomethyltrichlorosilane, hydrogen, methane and argon were studied by X-ray and selected area electron diffractometries. The SiC was identified to be 3C type, in which the stacking sequence of the closest packed layers is highly disordered along one of the [111] directions. Moreover, it was found that a decrease in hydrogen concentration or an increase in methane concentration enhances the orientation of these layers parallel to the fiber surface, and increases the crystallite size. Such changes in the orientation and the crystallite size are considered to be due to the increase in methane concentration in the reaction zone.

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炭素繊維に被覆した炭化ケイ素の結晶性

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モノメチルトリクロロシラン、水素、メタン、アルゴンの混合ガスから 1200°C に加熱した炭素繊維上に SiC を被覆し、被覆 SiC の構造、結晶性、配向性を X 線回折法によって調べた。その結果、SiC は最密充てん面の [111] 方向に沿う積層順序がかなり乱れた 3C 構造と同定された。更に、ガス中の水素濃度の減少、あるいはメタン濃度の増加によってこの面が繊維フィラメント表面に平行に配向するようになること、またそれに伴って結晶子が粗大になることを認めた。このような結晶子の配向性とサイズの変化は、メタンの過飽和度の増大に起因すると考えられた。

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1. Introduction

Carbon fiber-aluminum composite is possible to produce by a molten-metal infiltration technique, when the wettability of carbon fiber with molten aluminum is improved through a certain surface coating. However, such a surface coating is incompetent to prevent the serious degradation of strength which PAN (polyacrylonitrile)-based carbon fibers undergo by a reaction with aluminum¹⁾. To overcome this problem, we have studied the coating of carbon fibers with silicon carbide as the barrier against the reaction with aluminum²⁾, and in the course of this study it has been found that the coating when it deposited at below 1300°C has uniform thicknesses on every

filaments in the carbon fiber yarn. However, fuller information lacks on the crystallinity or closeness of the coating formed under such condition.

This paper will report the effect of hydrogen and methane concentration in the reaction gas on the crystal structure, the crystallinity and the orientation of silicon carbide coating deposited from monomethyltrichlorosilane on the carbon fibers.

2. Experimental

2.1 Apparatus for coating

The apparatus used for coating carbon fiber is shown in Fig. 1. The gases of reactants and

Fig. 1. Apparatus for coating. (a) CH_3SiCl_3 , (b) furnace, (c) carbon fiber yarn.

carrier were mixed in the line and flowed into the reactor. The flow rates of Ar and CH_3SiCl_3 were 250 and 1.6(STP)ml/min, respectively. H_2 and CH_4 were fed at several stages of rates from 0 to 70, and at rates 0, 0.4 and 1.4 ml/min, respectively. Ar, H_2 and CH_4 were of research grade of Matheson Co. CH_3SiCl_3 was of EP grade of Tokyo Kasei Kogyo Co.

The employed carbon fibers were TORAYCA T 300 and TORAYCA M 40, which are composed of 3000 and 6000 filaments, respectively, of ca. $6.5 \mu\text{m}$ in diameter. They were suspended in the center of a recrystallized alumina tube (Nippon Kagaku Togyo Co.; SSA-S) of 12 mm in diameter and heated at 1200°C . In order to avoid the contamination of the deposit by the alumina, the inside of the reaction tube was covered with SiC by flowing the reaction gas for two hours. The coating on the carbon fibers were carried out thereafter, for 30 min in each run.

2.2 Analysis

The coating on the carbon fibers were analysed for Si by a Molybdenum-blue method after decomposing the coated fibers by molten mixture of NaNO_3 and KOH. The coatings were identified and characterized by X-ray diffractometry and X-ray fiber diffraction photograph using $\text{Cu K}\alpha$ radiation generated from Rotaflex of Rigaku Denki Co. Selected area electron diffractometry (SAD) and transmission electron microscopic observation were made by HU-200E electron microscope of Hitachi, Ltd.

3. Results

3.1 Appearance of coating

Figure 2 shows the scanning electron micrograph of the cross section of the fibers coated at a H_2 flow rates of 10 ml/min. Each filament of the fiber is coated with film of equal thickness around

Fig. 2. Cross section of coated carbon fiber.

Fig. 3. Variation of Si content in the coating with flow rate of H_2 .

$0.5 \mu\text{m}$. Cross sections of fibers coated at other flow rates of H_2 and CH_4 were similar to this figure.

3.2 Composition of the coated films

The content of Si in the films coated in the absence of CH_4 addition is plotted in Fig. 3 against the flow rates of H_2 . The deficiency and the excess of Si from stoichiometric SiC composition are due to coexistence of free C and free Si, respectively. This figure shows that the film coated in the absence of CH_4 and at a H_2 flow rate of 7 ml/min has the SiC composition and this composition is maintained at H_2 flow rates up to 30 ml/min (the deviation from 70 wt% in this figure is thought to be experimental error). At a flow rate of 50 ml/min, a little amount of co-deposited free Si was detected by X-ray diffractometry.

3.3 X-ray diffraction

X-ray diffractometry was carried out on the fibers coated in gas mixtures with or without CH_4 , the X-ray beam being irradiated vertical to the fiber filaments on glass plates. The diffractograms are shown in Fig. 4.

Each peak was assigned to 3C polytype of

Fig. 4. X-ray diffractograms of the coated fibers. The first and the second values following the letters signify flow rates in ml/min of hydrogen and methane, respectively: (a): 5, 0; (b): 20, 0; (c): 50, 0; (d): 20, 1.4.

The letters C and Si in the figure denote the diffractions due to carbon fiber and co-deposited Si, respectively.

SiC, except the peaks ($d=2.67 \text{ \AA}$) marked with (x). The position of such marked peaks coincides with that of 10.0 diffraction of polytypes of 2H, 4H, etc. It should be noted here that the 200 diffraction does not appear or very weakly appears on these patterns as found by the previous investigations^{(4), (5)} on SiC films deposited at around 1200°C . These patterns in Fig. 4 show that diffraction lines are sharp when the coating was made at lower rates of H_2 in the absence of CH_4 (pattern (a)). They are broader at higher flow rates (patterns (b) and (c)), but even at a higher flow rate of H_2 they become sharper again by addition of CH_4 (pattern (d)).

In Fig. 5, the variation of the half-maximum breadth of 111 diffraction line is shown against H_2 flow rate for several amount of CH_4 addition. The size of the crystallites coated in the absence of CH_4 were estimated from the half maximum breadth of the 111 and 220 diffraction lines of powdered samples, and shown in Fig. 6 against H_2 flow rate.

X-ray fiber diffraction photographs on flat films are shown in Figs. 7(a)-(d). They correspond to

Fig. 5. Variation of the half-maximum breadth of 111 diffraction line of Cu $K\alpha$ radiation with flow rate of H_2 .

Fig. 6. Variation in crystallite size of the SiC coated at various flow rates of H_2 in the absence of CH_4 . $\circ$: estimated from 111 diffraction line, $\triangle$: estimated from 220 line.

the patterns (a)-(d) in Fig. 4, respectively. The film and the coated fiber specimens were placed vertical to the beam of Cu $K\alpha$ radiation collimated to 1 mm in diameter. The direction of the axis of the coated carbon fiber is the vertical in the figures.

Figure 7(a) is the pattern of the fiber coated at an H_2 flow rate of 5 ml/min. The pattern shows a pair of sharp intensity maxima on the horizontal in the Debye-Scherrer ring of the 111 diffraction of 3C SiC. This pattern shows that one of the [111] directions of each crystallite is oriented in a direction normal to the fiber axis, and the azimuthal orientation of the crystallites about the [111] is random. Moreover, a broad ring (breadth in $2\theta=5.3^\circ$) of weak intensity overlaps the diffraction maxima of 111 diffraction mentioned above. The intensity of this ring is

Fig. 7. X-ray fiber diffraction photographs of the coated fiber. The first and the second values following the letters signify flow rates in ml/min of hydrogen and methane, respectively : (a) : 5, 0; (b) : 20, 0; (c) : 50, 0; (d) : 20, 1.4.

The ring is due to 111 diffraction ($2\theta=35.7^\circ$) of 3 C SiC. The letters C and Si in the figure denote the diffractions due to carbon fiber and co-deposited Si, respectively.

strongest at the inner edge and becomes gradually weaker outwards. The diffraction angle of this inner edge coincided with that of the diffraction peak marked (x) in Fig. 4. This unsymmetrical distribution of the intensity across the ring will be discussed later.

Figure 7(b) is the pattern of the coating deposited at an H_2 flow rate of 20 ml/min. In comparison with Fig. 7(a), this shows slightly parallel orientation of the (111) plane to the fiber axis. At H_2 flow rate of 50 ml/min (Fig. 7(c)), the orientation disappears and Si co-deposits.

The pattern (d) in Fig. 4, and Fig. 7(d) are the diffractogram and the diffraction photograph of

the fiber coated in the same deposition condition as in the fiber of Fig. 7(b), except that 1.4 ml/min of CH_4 was added to the reaction gas mixture in the former case. These figures are practically similar to the patterns of (b) in Fig. 4 (b) and Fig. 7(b), respectively.

It is concluded from these observations that when the flow rate of H_2 is so low as to make free carbon deposit, coating is composed mainly of large crystallites of 3 C SiC with the (111) plane orienting parallel to the fiber axis, and that when H_2 flow rate is so high that the coating has SiC composition or contains free Si, the crystallites become smaller and the preferred orientation

Fig. 8. (a), (b), (c) : SAD patterns of the fibers coated at H₂ flow rates of 5, 20 and 50 ml/min, respectively, in the absence of CH₄.

(d-1), (d-2) : SAD patterns of the fiber coated at flow rates of H₂ and CH₄ of 20 and 1.4 ml/min, respectively. (d-3) : Dark field image with 00.3 diffraction in (d-1).

disappears gradually. The addition of CH₄ into the gas has the same effect on crystallite size and orientation as the decrease of H₂ flow rate has.

3.4 Electron diffraction

Because of high transmissivity of X-ray, it is impossible to determine the orientation of the (111) plane to the surface of the fiber, or to

discuss the structure of the crystallites. SAD from the skin of the coated fiber was employed to overcome these difficulties. For this, single filaments of the coated fibers were set vertical to the electron beam in the transmission electron microscope operated at 175 kV.

Figures 8(a) and (d-1) are the SAD patterns of

the coated fibers correspond to Figs. 7(a) and (d), respectively. The surface of the filament lies vertical to the figure plane and parallel to the arrow drawn in each figure. These two patterns seem to be essentially identical. As Fig. 8(d-1) typically shows the feature of the patterns, we will discuss on this figure.

The pattern was indexed with hexagonal indices. The relationship between the hexagonal indices and the cubic indices is shown in Fig. 8 (d-2). It is apparent from this figure that diffractions on 00. *l* and 11. *l* rows are discrete spots, while those on 10. *l* and 20. *l* rows heavily streak along individual rows. Main spots, including the streaked ones, can be indexed on the basis of 3C structure as shown in Fig. 8 (d-2). Since the (00.3) (in hexagonal index) (by cubic index (111)) planes of 3C SiC corresponds to three different kind of closest packed layers composed of carbon and silicon atoms⁶⁾, the streaking along the 10. *l* and 20. *l* rows means that the stacking sequence of these layers is highly disordered. Discrete spots on the 00. *l* and 11. *l* rows also support the idea that the stacking sequence of the closest packed planes are disordered, because it is such a disorder that conserves the planes related by $h-k=3n$.

It is possible that these coating contains "one-dimensional disordered" SiC, the structure of which was disclosed by Shinozaki et al.^{8),9)}. Moreover, since this figure shows some minor spots in the streak, it might be thought that a trace of some longer-period polytypes is included. But it is also possible that such spots can be arisen from the crystallites misoriented to the fiber surface.

Dark field image with 00.3 (in hexagonal index) (or 111 in cubic index) diffraction are shown in Fig. 8(d-3). Bright column of *ca.* 200 Å in width extending to *ca.* 1000 Å perpendicularly to the surface are the single domains in which the above mentioned double layers stack.

Figure 8(b) is the SAD pattern of the fiber which gave the X-ray diffraction patterns (b) in Fig. 4 and Fig. 7(b). It is seen that slight orientation of (00.3) (or (111)) plane is observed. The streaks are not seen in this pattern. In Fig. 8(c), which is the pattern of the coating formed at 30 ml/min of H₂, the orientation and the streak disappears. In both of the Figs. 8(b) and (c), no 200 diffraction is observed, as in the X-ray diffraction patterns.

4. Discussion

4.1 Effect of H₂ or CH₄ in the reactant

As the result of the present study shows, the orientation of one of the {111} planes of 3C SiC becomes eminent and the crystallite size becomes larger when the amount of H₂ decreased or CH₄ was added in the gas mixture.

According to the thermodynamical calculations^{3),12)} on the equilibrium composition of gas in a system comprised of C, Si, Cl and H, the stable species containing Si or C are SiCl₂, SiH₃Cl and CH₄ at around 1200°C. Therefore, the process of forming SiC, C and Si can be illustrated as follows :

($\langle \text{Si} \rangle$ and $\langle \text{C} \rangle$ denote Si and C-bearing intermediates adsorbed on the surface.)

These equations suggest, that H₂ addition cause the lowering in supersaturation of CH₄ (or concentration of $\langle \text{C} \rangle$) by the equilibriums (2) and (3). Addition of CH₄ will increase the supersaturation of CH₄ again.

Therefore, the result mentioned above means that the supersaturation of CH₄ (or the concentration of C-bearing intermediates) controls the size and orientation of the crystallites.

The estimated crystallite size (Fig. 6) shows that the crystallites formed at 25 ml/min of H₂ flow rate are *ca.* 40 Å in size in both [111] and [220] directions, while the crystallites formed at 2 ml/min are 300 and 180 Å in these directions, respectively.

Accordingly, it is concluded that CH₄ promotes both the vertical and the in-plane growth of the oriented (111) plane in comparison with the nucleation. It is known that a preferred orientation of the crystallites in a coating can be occurred by the preferred oriented nucleation as in the case of epitaxial growth or by the rapid growth of a particular plane. From the present results we can not decide which is the case. In the latter case¹⁰⁾, however, the coating should be random in orientation when the coating thickness is in the range of some μm, judging from the result of previously reported study. Therefore, we think that the orientation of the coating may result from the oriented nucleation at the begin-

ning of the coating.

4.2 Effect of disordered structure on the diffraction pattern

The X-ray and the electron diffraction patterns did not show the 200 diffraction of 3C SiC. As shown in Fig. 8(d-2), the planes of $\{200\}$ are converted only to $\{10.2\}$ by the hexagonal lattice. Since the diffractions due to these planes are streaked, this will give weak background in the X-ray diffraction pattern and the SAD pattern of randomly oriented crystallites. Other groups of planes in this figure contain planes which are converted to planes with hexagonal indices related by $h-k=3n$. Since diffraction due to such planes are discrete spots, it is thought that they have shown definite peaks in the X-ray diffraction.

Therefore, the absence of the 200 diffraction peak can be a criterion of the disordered stacking structure. Thus, the absence of this diffraction in Figs. 4, 7, 8(b) and (c) indicates that these crystallites are also one-dimensionally disordered.

Though the peaks marked (x) in Fig. 4 can be due to 10.0 diffraction of α -polytypes, such as 2H or 4H, no peaks due to other diffractions expected for these polytypes are observed. Therefore, this peak is considered to be arisen from the streaks passing through the 10.0 point as shown in Figs. 8(a), (d-1) and (d-2). The broad tails following this peak observed in Figs. 4, 7(a) and (d) will also arise from these streaks, as reported for the origin of an unsymmetrical Debye-Scherrer ring of random-layered carbon¹¹⁾.

According to Shinozaki et al.⁸⁾, one-dimensional disordered SiC itself is composed of randomly stacked 3C-phase and α -type-phases lamellae, the contents of which vary with materials. Therefore, in addition to 3C-phase which is considered to be an important contributor to the intensity modulation of the streaks in Figs. 8(a), (d-1) and (d-2), it is probable that α -type-phases make some contribution to these streaks.

5. Summary and conclusion

The crystallinity and orientation of SiC coated from CH_3SiCl_3 on carbon fiber at 1200°C was investigated and the following conclusions were obtained:

(1) The content of free carbon in the coating increased with decreasing amount of H_2 in the reaction gas.

(2) The deposited SiC has 3C polytype structure in which the stacking order of the closest packed layers composed of carbon and silicon atoms is highly disordered along one $[111]$ direction.

(3) The decrease in the amount of H_2 or increase in CH_4 in the reaction gas makes the SiC crystallites large in three dimensions, and makes the planes of the closest packed layers parallel to the fiber surface.

(4) The change in the amount of H_2 or CH_4 is considered to change the supersaturation of CH_4 in the reaction zone. This will cause the change in the orientation and the crystallinity of the SiC crystallites.

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