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Formation and Characterization of Silicon Carbide Whiskers by Acheson Method

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에치슨법에 의한 탄화규소 휘스카의 성장과 특성분석

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ABSTRACT

Whiskers of SiC were grown from the mixture of silica and graphite powders by Acheson method(direct heating method). The structural, morphological and chemical characterizations have been performed by X-ray diffractometer(XRD), transmission electron microscopy(TEM), optical microscopy (OM), scanning electron microscopy(SEM), X-ray photoelectron spectroscopy(XPS) and energy dispersive spectrometer(EDS). The growth mechanism of SiC whiskers is also discussed.

요 약

실리카와 흑연분말의 혼합체로 부터 에치슨법을 이용하여 탄화규소 휘스카를 성장시켰다 성장된 탄화규소 휘스카의 구조적, 형상학적, 화학적 특성 분석을 x선 회절분석, 투과전자현미경, 광학현미경, 주사전자현미경, X-ray photoelectron spectroscopy(XPS), energy dispersive spectrometer(EDS)를 이용하여 행하였다. 분석결과를 이용하여 탄화규소 휘스카의 성장기구를 고찰하여 보았다.

INTRODUCTION

Silicon carbide (SiC) whisker is widely used as one of the best reinforcements for various composite materials because of its mechanical strength as well as its excellent resistance to heat and chemicals. Reinforcement of glasses[1] and ceramics[2] by silicon carbide whiskers resulted in up to fourfold and twofold improvements, respectively, in strength and fracture toughness. Other advantage of SiC whisker is that its decomposition temperature at one atm. is around 2800℃ and is stable up to 1500℃ at normal condition.

Growth methods of SiC whiskers, which have been employed previously, are classified to four categories : (1) vaporization method[3,4], (2) chemical vapor deposition (CVD) process[5-8], (3) vapor-liquid-solid (VLS) process[9,10] and (4) thermal decomposition method of rice hulls[11,12]. These methods used different source materials and different reactions from each other, but they employed the same range of growth

temperature of 1300° to 1600℃ and the same atmosphere of reduction. However, the CVD and VLS processes should use high-cost gas sources and the vaporization and rice hull method endures low yields.

Composites produced with different commercial SiC whiskers resulted in different fracture toughnesses[9]. It is not obscure that this fact is due to the intrinsic properties or the extrinsic properties(i.e. whisker/matrix interface property) of SiC whiskers, but the reinforcing behavior might be possibly affected by the intrinsic properties. The intrinsic properties of whiskers such as crystal defects, chemical purity and surface condition are not free from influences of growth method

The research program from which this paper is derived has concentrated on the growth and characterization of SiC whiskers using Acheson method, which has been widely used to produce SiC powders. This growth method costs cheaper than other methods such as CVD and VLS processes, since it uses cheaper raw materials such as low-grade powders rather than the expensive gas sources. Vaporization method used by Knippenberg and Verspui[3,4] employed hydrogen atmosphere, but the present method was done in air, actually in CO atmosphere due to oxidation of C. The morphological, structural and chemical characterizations of the grown whiskers were conducted using optical microscopy (OM), scanning electron microscopy (SEM), X-ray diffractometer (XRD), X-ray photoelectron spectroscopy (XPS), energy dispersive spectrometer (EDS), and transmission electron mcroscopy(TEM).

EXPERIMENTAL PROCEDURES

A laboratory-scale Acheson furnace, 680mm×600mm×480mm, was built in-house. A rod-shaped heating element, 15mm diameter and 300mm length, was made of graphite Its diameter was reduced to 10mm with 100mm length around a center to produce heat around central area of furnace. A graphite cylinder, 15mm ID×35mm OD×200mm, was inserted on a heating element both to protect a heating element from reacting with source materials and to provide sites for SiC whiskers to grow on. Temperature near a heating element in a furnace was measured by optical pyrometer through a graphite viewing pot, which was cylinderically-shaped tube and of which an outside end was cooled with a cooling water jacket.

The composition of raw materials was similar to that of production of SiC powders: 60wt% SiO_2, 30wt%C, 5wt% sawdust and 5wt% NaCl. Mole ratio of C/SiO_2 of raw materials was 2.58 Since 1 mole of SiO_2 needs 1 mole of C to produce 1 mole of SiC, the overall reaction condition is carbon-rich. Excess carbon reacts with oxygen and produces CO gas during the reaction. The by-product CO gas keeps a reduction atmosphere inside the furnace and thus protects the heating element from oxidation. Sawdust is imperfectly burned and produces CO gas at low temperature before SiO_2 powder begins to react with C powder. The resulting CO gas makes a reduction atmosphere in the initial stage of reaction as well as a path for by−product gases to flow out NaCl, added as raw material, decomposes, reacts with impurities and produces halogen compounds, which are removed as a by−product gas.

All of the raw materials were powders with particle size of less than 1mm diamter The raw material powders were mixed for 2hrs using V-type mixer and then loaded in the Acheson furnace. The furnace was heated to and kept at 1500℃ for 8hrs.

The size, surface morphology and cross-sectional shape were studied with optical microscopy and SEM* A number of whiskers were removed from the whisker wool and placed in suspension in methanol. The suspension was applied on a slide glass. To make SEM specimen, the dispersed whiskers on glasss slide were coated with Au.

The growth shape, growth direction and growth defects were observed by TEM= operating at 160 KV of acceleralating voltage. TEM specimen was prepared

by applying the dispersed specimen onto a porous carbon film, supported on a Cu grid. The camera constant was 104cm, which was corrected by Au diffusion pattern. Dark field and bright field images and SADP of whiskers were obtained by TEM analysis.

Crystal structure of SiC whiskers were determined by X-ray diffractometer and chemical composition and impurity content were evaluated with XPS+. The determination of chemical composition in a small area of sample was performed by EDS*.

RESULTS AND DISCUSSION

Whisker growth-After the reaction at 1500℃ for 8 hrs was over and the furnace was cooled down, it was found that an oval-shaped cavity of~5cm diameter was formed around a graphite cylinder. It should be formed by the volume shrinkage, which occurred due to discharge of gases from reaction of raw materials as well as to a partial sintering of raw material powders. Since the temperature near the heating element was higher than that of the other places, the cavity was formed around it.

A piece of whisker wool, thickness of 4mm and length of 60mm, was produced on the lower half of the graphite cylinder, which was inserted on the heating element. It was easily taken off from the graphite cylinder. Since the cavity was formed around the heating element, a piece of whisker wool didn't contact with raw material powders, that is, a space between whiskers and powders was created. Most of the grown SiC whisker wool colored pale-green, but a part of whisker wool near the graphite cylinder had a few black particles and colored dark-green.

*JSM 840A with LINK AN10-95S, JEOL LTD., Tokyo, Japan.

#JEM 200CX, JEOL LTD., Tokyo, Japan.

+PHI Model 548, Perkin-Elmer corporation, Eden Praire, MIN, USA.

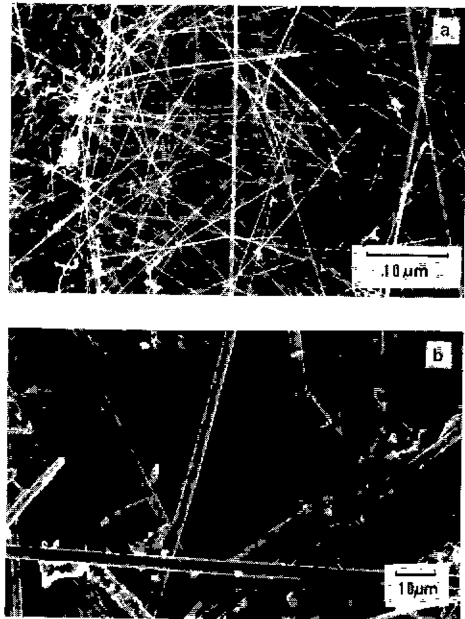

Fig.1. SEM micrographs of as-grown SiC whiskers (a) with pale-green color and (b) with dark-green color.

Morphological analysis-Whiskers got all tangled up like wool, but the detached whiskers from wool were easily dispersed in methanol. OM observation resulted that the ranges of diameter and length of whiskers were 0.1-5.0μm and 20-300μm, respectively. The size range of whiskers is similar to that grown by other methods.

SEM micrographs show that the pale-green whiskers(Fig.1a) are thinner and have less particles than the dark-green ones (Fig.1b). Surface of both colored whiskers was smooth. The cross-sectional shape of most of thin SiC whiskers is a truncated and smoothed triangle (indicated by arrows) as seen in Fig 2, while thick whiskers seem to be round. It indicates that the growth direction is [111], a normal growth direction of SiC whiskers. The cross-sectional shape is identical to that of whiskers, which is observed in a cross-section of an ceramic matrix composite[13]. But whiskers with a hollow cross-section, which were often observed in the commercialized SiC whiskers and whiskers grown by other

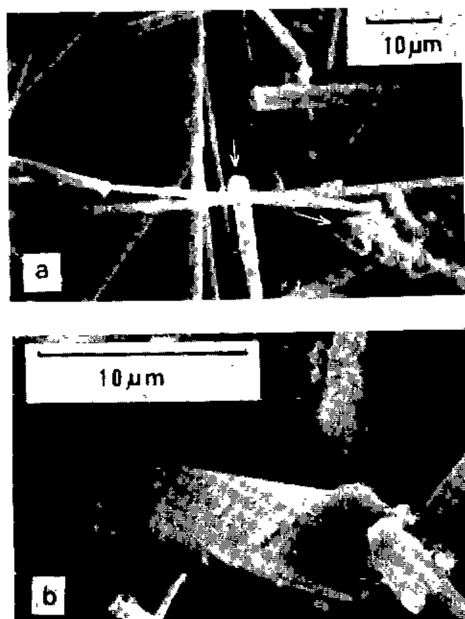

Fig.2. SEM micrographs showing the cross-sections of SiC whiskers.
(a) A low magnification micrograph. Arrows indicate a truncated and smoothed triangle of the cross-section and (b) a high magnification micrograph.

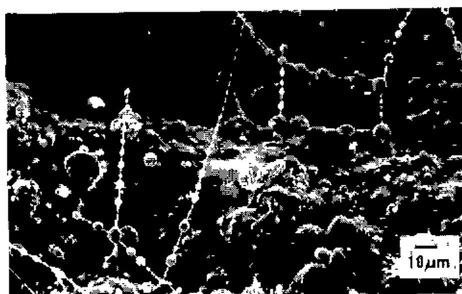

Fig.3. SEM micrograph of rosary-like whiskers, which were grown near melt.

methods, were not founded.

A very special shaped, that is, a rosary-like shaped whiskers were found, as seen in Fig.3. This type of whiskers also observed in SiC whiskers grown in a fluorosilicate melt by Saito and Yamai[11]. The rosary-like shaped whiskers were grown on a melt film, which was formed at the uncovered region of heating element. Possible composition of the melt, formed during reaction, is not SiC but silica or silicon, since the reaction temperature was around 1500℃. And thus the melt should be a silicon-rich phase and thus we can say that the rosary-like whiskers were grown on the silicon-rich melt. The growth condition of rosary-like whiskers is the same as that suggested by Saito and Yamai. But it is hard to explain the growth mechanism of rosary-like whiskers at this point. However, small balls on a melt film are similar to SiO_2 particles found in the pore of the refractory concrete by Chou and Ko[15]. They also found SiC whiskers in that pore. If balls were to be SiO_2 glass with metallic impurities such as Fe, Al and Ca, SiC vapors are resolved into them and SiC whiskers will grow from balls above the solution limit. And since the density of balls are so high on surface of melt, the grown whiskers connect balls like a rosary.

XRD analysis-Diffraction spectra of the dark-green and the pale-green whiskers obtained using XRD are shown in Fig 4a and b, respectively. Both whiskers are cubic-type β-SiC and have a small amount of silica, of which a peak appears at $2\theta=27°$. However, the pale-green whiskers have relatively less amounts of impurities than the dark green whiskers. The dark-green whiskers were washed with methanol to remove a few black particles and taken with XRD,

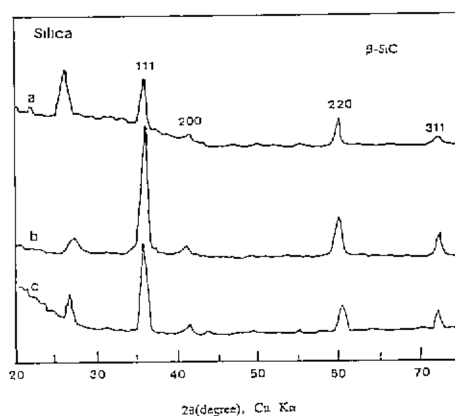

Fig.4. XRD spectra of SiC whiskers (a) with dark-green color, (b) with pale-green color and (c) washed with methanol.

but some of impurities were still remained, as shown in Fig.4c. This implies that the grown SiC whiskers contain silica as an impurity.

The dark-green whiskers washed with methanol were etched with HF for 30 min and then XRD spectrum was again obtained. A peak at $2\theta=27°$ was reduced, but a trace is still remained (Fig.5a). This indicated that silica was mixed with SiC like a complex Si-O-C phase, which was found in inclusions of whiskers by Nutt[16], on whisker surface. And thus the HF-etched whiskers were oxidized at 900℃ in air for 8 hrs to remove it. XRD pattern of the oxidized whiskers shows an increase of a peak of silica, as seen in Fig.5b. After the oxidized whiskers were etched with HF for 30 min, a peak of silica was disappeared (Fig.5c). The oxidation process changed a mixed surface layer of silica and SiC as well as pure SiC layer near surface into pure SiO_2 layer, which was easily removed by the subsequent HF etching. It is hard to believe that this mixed surface layer was formed during reaction at 1500℃. They might be condensated on whisker surface from mixed vapor species evaporated and still unreacted in the furnace,

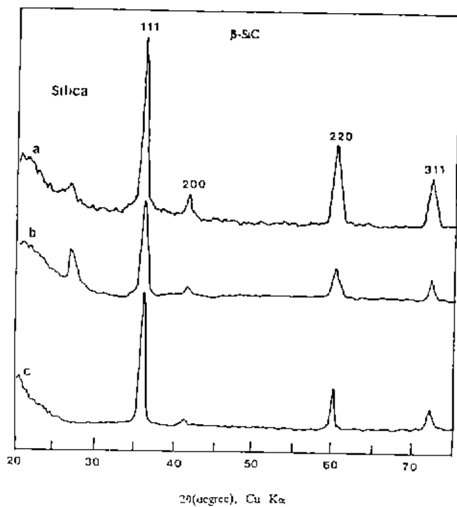

Fig.5 XRD spectra of the whiskers : (a) HF-etched for 30min, (b) oxidized at 900℃ for 8hrs and (c) oxidized at 900℃ for 8 hrs and HF-etched for 30min.

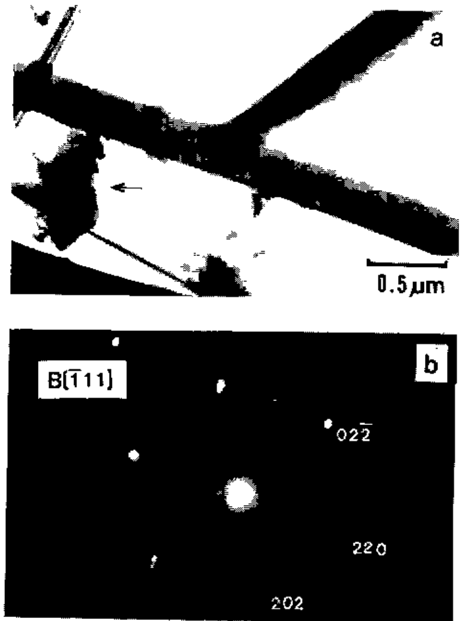

Fig 6. TEM micrographs showing (a) bright field image of whiskers and plate-like fine particles and (b) SADP of a paticle indicated by an arrow in (a).

when the furnace was cooled down.

After whiskers were washed, a few fine particles were still distributed in whiskers Fine particles mixed in whiskers, as seen in Fig.6a, were observed by TEM A shape of particles is plate-like. Selective area diffraction pattern (SADP) of a particle (indicated by arrow) proves that it is not silica but β-SiC. This result supports that impurity such as silica are on surface of whiskers.

XPS analysis-XRD results suggest that the grown whiskers contain impurity such as silica on their surface To examine this, XPS was employed for four samples the first sample was an as-grown whiskers, the second HF-etched for 30 min, the third oxidized at 700℃ for 9hrs and the other oxidized at 700℃ for 9 hrs and HF-etched for 30 min. And XPS spectra of these samples are denoted by (a), (b), (c) and (d) in Fig 7, 8 and 9, respectively.

Firstly, a low resolution (band pass energy=100eV) survey scan was performed in the binding energy(BE)

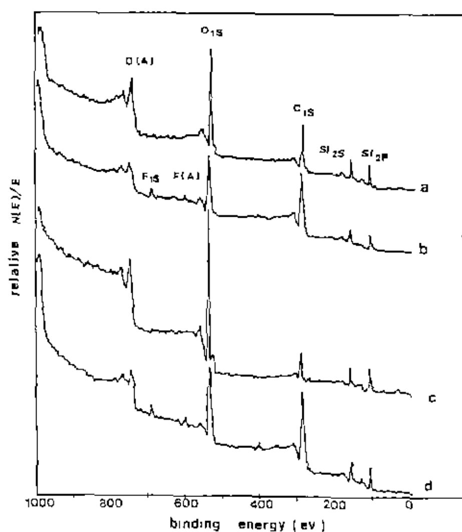

Fig.7. XPS spectra of a low resolution (band pass energy=100 eV) survey scan in the BE range of 0 to 1000 eV for SiC whiskers (a) as-grown, (b) HF-etched for 30 min, (c) oxidized at 700℃ for 9hrs and (d) oxidized at 700℃ for 9hrs and subsequently HF-etched for 30min.

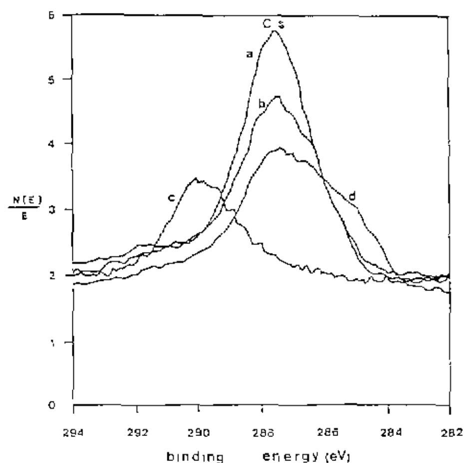

Fig.8. High resolution XPS spectra for C 1s of SiC whiskers (a) as-grown, (b) HF-etched for 30 min, (c) oxidized at 700℃ for 9hrs and (d) oxidized at 700℃ for 9hrs and subsequently HF-etched for 30min.

range of 0 to 1000eV, as seen in Fig.7. Major detected elements are Si, C and O. Measured value of the BE of each detected element is shifted to higher value from the standard value[17] of each element, since samples were charged by X-ray source of XPS.

For an accurate measurement, a sample should be exposed to the electron flood gun (EFG) in order to protect from accumulating charges. But since the whisker sample is composed of very fine whiskers and its density is low, it is difficult for EFG to shower electrons on fine whiskers uniformly. And thus XPS spectra was obtained without a compensation of build-up charges by EFG. However, since a shifted value for each element is almost a constant at the same analyzing condition, results from XPS spectra are the same. Possible impurities such as Fe, Al and Na were not detected and thus concentrations of these impurities were less than the detection limit of XPS, ~1%.

HF-etching process reduced the intensity of oxygen in XPS spectrum, that is, removed oxygen on surface, but oxygen cannot be completely removed (Fig.7b) Oxidizing process increased the intensity of oxygen (Fig.7c), while the oxidizing and etching process returned spectrum to the original(Fig 7d).

Secondarily, high resolution XPS measurement for an as-grown and three differently-treated samples were recorded with 20 pass scans in the energy ranges of C 1s and Si 2p around 287 eV and 104 eV, respectively. The resulting spectra for C 1s and Si 2p are shown is Fig.8 and 9, respectively. The BE of C in hydrocarbon or free C is higher than that in SiC. The BE of XPS peak of sample oxidized at 700℃ is shifted to higher energy value of 288.8 eV, while those of other samples are at the same BE level, 287.5 eV. The energy difference between two peaks is 1.3 eV(The standard energy difference between peaks for C of Si-C bonding and of free C is 1.7 eV.). This result implies that most of C on surface were changed to CO or CO_2 and discharged during oxidation and the rest of C remained on the surface as free C or hydrocarbon. Since the BE of hydrocarbon is higher than that of free C, a peak at 288.8 eV should be due not to hydrocarbon but to free C. And also

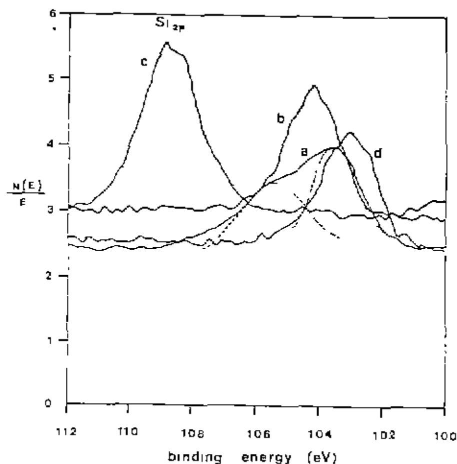

Fig.9. High resolution XPS spectra for Si 2p of SiC whiskers (a) as-grown, (b) HF-etched for 30 min, (c) oxidized at 700℃ for 9hrs and (d) oxidized at 700℃ for 9hrs and subsequently HF-etched for 30min.

hydrocarbon is not an intrinsic component but an absorbed species on surface of whisker. This result implies that although an oxidized sample has a free C layer on surface, as-grown and two etched samples have no C layer.

The BE of Si 2p for Si-O bonding is higher than for Si-C bonding The Si 2p peak of the oxidized sample is shifted to the higher energy level(Fig.9c), while others(Fig.9a, b and d) are in the similar level. A little misfit of three peaks seems to be originated from difference of the build-up charge of samples. The same reason may make more difference(4.8 eV) in BE between Si-O bonding and Si-C bonding than the standard difference(1.0 eV), since SiC is a semiconductor and SiO_2 is an insulator The peak of an as-grown sample is broad and can be resolved into two subsidiary peaks(dotted curves in Fig.9a) : a primary peak is at 103.3eV and a secondary peak at 105.7 eV. The difference of BE is 2.4eV and much higher than the standard difference of 1 0 eV. This is also due to the build-up charge. A secondary peak for Si-O bonding at 105.7 eV is less than a primary peak for Si-C bonding at 103.3 eV, but this implies that as-grown SiC whiskers contain much silica. XPS spectrum for HF-etched sample(Fig.9b) is broader than that for an oxidized and etched sample(Fig.9d), but it is not easily resolved like that for an as-grown one. However, SiC whiskers, only HF-etched for 30 min, have less silica than an as-grown one, but they have more silica than an oxidized and etched sample. And thus surface of the oxidized sample was covered with SiO_2 and those of an as-grown and an etched samples were partially covered with SiO_2, while the oxidized and etched sample had little oxide. The results from XPS analysis are consistant with those from XRD.

SEM/EDS analysis-SEM micrograph revealed that whisker had a spheres at the growing tips(Fig.10). The presence of spheres at the tips indicates that whiskers were grown by the vapor-liquid-solid mechanism suggested by the previous researches[9,10,18]. The diameters of a whisker and a sphere were around 10μm and 20μm, respectively. The messy periphery of spheres is similar to that observed in twinned β-SiC whiskers by de Jong and McCauley[19] rather than that in whiskers from rice hulls by Milewski et al[10]. Since whiskers are under the lateral thickening process in the VLS mechanism instead of the axial extension process, whiskers seem to be thick and their periphery is messy.

EDS spectra obtained on a sphere(denoted by M) and a whisker(denoted by N) are shown in Fig.11a and b, respectively. EDS spectrum of a whisker shows

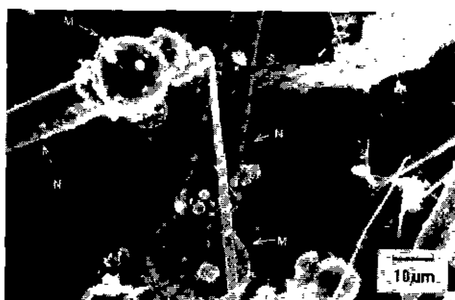

Fig.10. SEM micrograph of whiskers having a sphere at the growing tip.

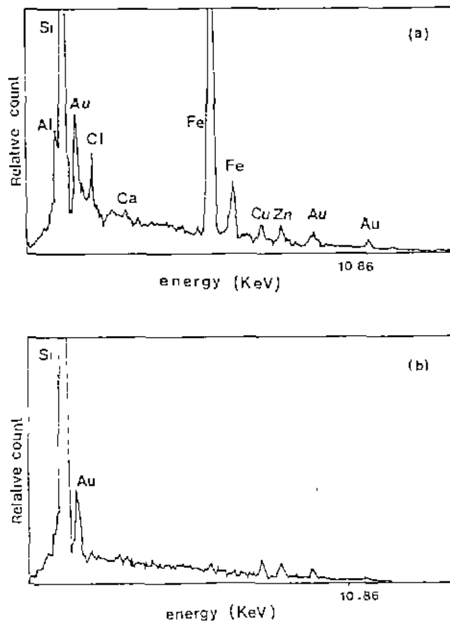

Fig. 11. EDS spectra of (a) spheres (denoted by M in Fig. 10) and (b) trunks (denoted by N in Fig. 10) of the whiskers.

that a whisker has only Si, that is, it might be pure above the detection limit of EDS. Light elements such as C and O cannot be detected by EDS. The detected elements such as Au, Cu and Zn should be originated from Au-coating of sample and a sample holder of brass.

But Si, Fe, Al, Cl and Ca were detected in a sphere, especially a large amount of Si and Fe. A sphere seems to be a collector of impurities. Although no Fe was added intentionally to raw materials, Fe in the raw materials such as silica and carbon might be aggromerated and melt to a sphere during reaction. As mentioned before, a sphere might be Fe-rich SiO_2 glass phase resolved with C. Chou and Ko[15] indicated that no SiC whiskers were found if the refractory concrete specimen containing metallic silicon and coal tar pitch was fired in a reducing atmosphere. This means that oxygen might play an important role in growing whiskers. Nutt also found the presence of oxygen in the whisker core-region using energy loss spectra (ELS). The role of oxygen in the growth of

Fig. 12. SEM micrograph of whiskers, which lift balls at the initial stage of the whisker growth.

whiskers will be discussed in the end of this section.

Other interesting SEM micrograph, as seen in Fig. 12, shows the initial stage of growth of whiskers obtained by another short heating after the grown whiskers were added with raw materials in Acheson furnace. The size and periphery of sphere are smaller and cleaner than those of sphere shown in Fig. 11, because whiskers in Fig. 12 are in the growth stage of the axial extension in the VLS mechanism. Smooth surface of whiskers looks to be corroded by small spheres. The added whiskers might be coated by SiO_2 glass phase balls at low reaction temperature, and then if they were heated to higher temperature, SiC whiskers were vaporized and resolved into the Fe-containing glass phase. Above the solution limit, the growing SiC whiskers lifted glass phase balls, as seen in Fig. 12

TEM analysis-Structural information such as structural defect and individual morphology of SiC whisker was obtained by TEM. Most whiskers were straight and contained a large number of planar stacking faults either oblique against (Fig. 13a) or normal to (Fig. 13c) the growth axis. Most of whiskers had oblique faults. This observation is very similar to that from whiskers grown by other methods[12,18,20,21] The oblique faults occur on the other planes of {111} except of plane normal to the growth direction.

The stacking faults normal to the growth direction show hexagonal planes. The dark imaged hexagonal planes are the regions of stacking {0001} planes of 6H

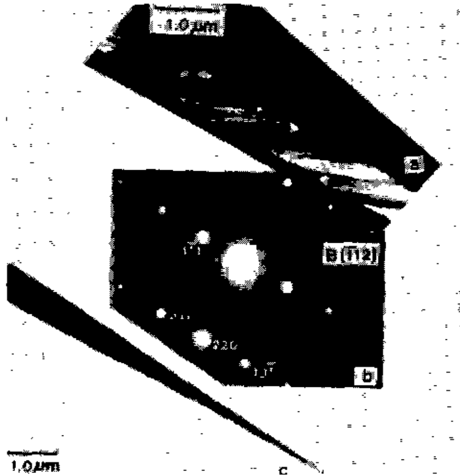

Fig.13. TEM micrographs and SADP of whiskers : (a) dark-field image of whiskers having oblique stacking faults, (b) SADP of both whiskers and (c) bright-field miage of whiskers having perpendicular stacking faults.

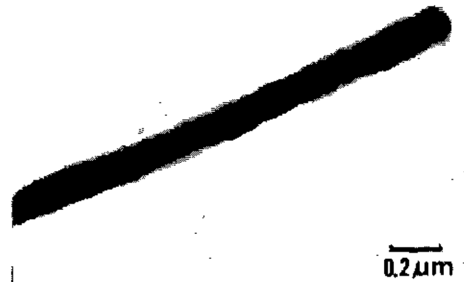

Fig 14. TEM micrograph of a whisker having surface layer.

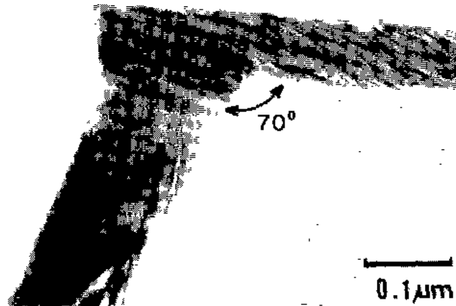

Fig.15. TEM micrograph of a whisker having two growth directions.

-SiC diffracted by the incident electron beam, while the regions of stacking {111} planes of β-SiC are gray -imaged. The whiskers having this type have a gradual decrease in a diameter and the smooth surface.

Analysis of electron diffraction patterns (Fig.13b) allows the whiskers to be identified as β-SiC, consistant with XRD results. And the growth direction of SiC whiskers are also confirmed to be <111> However, from SADP it is hard to detect microtwins, suggested by van Torne[21], stacking of 6H-SiC and many inclusions of a complex phase observed by Nutt. A pausible reason is that a volume of these defects is small.

Careful examination showed two interesting TEM morphologies of SiC whiskers ; the first whisker showed thin layer on surface (Fig.14) and the second a joint of two whiskers having different growth directions(Fig.15). The first one has heavy defect concentration and rough surface. Its structure was identified to be β-SiC by SADP. According to two oblique lines declined from a center to both sides, the cross-section of whisker might be triangle. Surface layer might be amorphous SiO_2, but it is not identified. It is also possible that it might be carbon film on Cu grid for TEM sample. Futher research will be required to identify it.

The second one(Fig.15) shows that an angle between two whiskers is 70°, which is an angle between two (111).planes (accurate angle is 70.5°). This indicates that the growth direction of both whiskers is <111>. The upper whisker has a lot of oblique stacking faults, of which planes are normal to the growth direction of the lower whisker. On the other hand, the lower one has few stacking faults near the joint, but it has heavier stacking faults and dislocations in the other places.

Growth mechanism-The grown whiskers were believed to be grown by the VLS mechanism primarily because of the presence of spheres at the tips of whiskers (Fig.10 and 12) and the lack of the axial

screw dislocation. Thin whiskers have a truncated and smoothed triangle cross-section(similar to hexagonal shape), while thick whiskers show a round cross-section. This means that the growth are composed of two stages: an axial extension and a lateral thickening. This is another evidence for the VLS mechanism.

Nutt proposed the two-dimensional VLS mechanism, of which the main idea was originated from microcrystalline inclusions distributed in the core-region. This mechanism can explain successfully the distribution of partial dislocations and the abundance of planar defects. But this mechanism is hard to explain the growth mechanism of inclusion-free region and the role of spheres at the growth tips of whiskers.

In the VLS mechanism, a catalyst sphere such as Fe is formed at the interface between solid(whisker) and SiC vapor source. A catalyst sphere is composed of pure metallic element, in which Si, C and/or SiC vapor are resolved. In the present work, we found that a sphere is not a pure metallic phase but possibly an oxygen-containing glass phase. Impurities such as Fe, Ca, Al and Cl might help to from a glass phase at low temperature. The Si-O-C mixed phase of a sphere might be precipitated and crystallized to microcrystallines, which provide heteroepitaxial nucleation sites for SiC single crystal. The heteroepitaxial nucleation might be the source of the abundant planar defects of whiskers.

CONCLUSION

SiC whiskers were grown by a direct reaction of silica and carbon using Acheson furnace. XRD and SADP showed that the grown whiskers were β-SiC of zinc blend structure and the growth direction was <111>. OM and SEM analyses revealed that the range of diameter and length of whiskers were 0.1-5.0μm and 20-300μm, respectively.

Impurity in whiskers was silica, which was mostly located on surface of SiC whiskers and thus were able to be removed by oxidation and etching process.

TEM analysis revealed that most of whiskers had a large number of planar stacking faults, which were prevalent on {111}, either normal to or ~20° oblique against the growth direction.

SEM/EDS observation revealed that a few of whiskers had spheres of glass phase at the growing tips. Whiskers are believed to be grown by the VLS mechanism.

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