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Mechanical Properties of Chemical-Vapor-Deposited Silicon Carbide using a Nanoindentation Technique

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ABSTRACT

The mechanical properties of silicon carbide deposited by chemical vapor deposition process onto a graphite substrate are studied using nanoindentation techniques. The silicon carbide coating was fabricated in a chemical vapor deposition process with different microstructures and thicknesses. A nanoindentation technique is preferred because it provides a reliable means to measure the mechanical properties with continuous load-displacement recording. Thus, a detailed nanoindentation study of silicon carbide coatings on graphite structures was conducted using a specialized specimen preparation technique. The mechanical properties of the modulus, hardness and toughness were characterized. Silicon carbide deposited at 1300°C has the following values: E=316 GPa, H=29 GPa, and K_c=9.8 MPa $m^{1/2}$; additionally, silicon carbide deposited at 1350°C shows E=283 GPa, H=23 GPa, and K_c=6.1 MPa $m^{1/2}$. The mechanical properties of two grades of SiC coating with different microstructures and thicknesses are discussed.

Key words*: *Silicon carbide, Nanoindentation, Hardness, Modulus, Fracture toughness

1. Introduction

Silicon carbide prepared by chemical vapor deposition has good mechanical properties, such as high hardness, moderate strength, good strength retention to high temperature, and corrosion resistance.[1-3] These properties make silicon carbide films attractive from both scientific and engineering points of view. Silicon carbide exists in cubic form, which is termed the beta form, and in a variety of hexagonal and rhombohedral modifications collectively termed the alpha form. The alpha forms of silicon carbide exists above 1800°C while the beta form of silicon carbide exists under 1800°C.[3] In order to fabricate silicon carbide films, many types of chemical vapor deposition techniques were adopted and single crystal, polycrystalline, and amorphous silicon carbide films were successfully deposited on a silicon substrate. Silicon carbide films are suitable for high-temperature, high-power or frequency micro-electromechanical systems (MEMS) and have been utilized as a micro-actuators, fuel atomizers, and resonators.[4]

Chemical vapor deposited silicon carbide films can also apply to tri-isotropic (TRISO)-coated fuel particles for use in a high-temperature gas cooled reactor. TRISO-coated fuel particles are surrounded by four layers: porous pyrolytic carbon (PyC), dense PyC, silicon carbide, and an outer dense PyC layer. In the fusion reaction, the mechanical property of the silicon carbide is of crucial importance. Under an irradiation test, TRISO-coated fuel particles are subjected to a number of forces that induce stress on the TRISO coatings. One of the recognized failure mechanisms is overpressure due to the generation of fission gas during the reaction. The overpressure exerts tensile stress on the PyC and silicon carbide layers. It is considered that the mechanical stability of the silicon carbide layer is of importance for the reliable design of fuel particles.[5-7]

Measuring the mechanical properties of the film is one of the crucial technical issues because the effect of the microstructure and length scale prevails for small-scale specimens. Therefore, it is necessary to adopt proper testing methods to determine the mechanical properties of films. Accordingly, several specialized testing methods have been developed. The most common techniques for measuring the mechanical properties of films are nanoindentation, micro-tensile testing, bulge testing, and micro-beam bending.[8-10] Nanoindentation can be used for the measurement of the hardness and modulus of films without an additional micro-machining process. The advantages of the nanoindentation technique include its simplicity in the preparation of the testing specimen and the versatility of the testing results. Recently, the nanoindentation technique has become widely used to characterize the mechanical properties of films and small-scale structures.[11-17]

In this study, silicon carbide films were deposited onto a graphite substrate and the mechanical properties of the films were characterized by a nanoindentation technique. In order to fabricate the silicon carbide films, low-pressure chemical vapor deposition was used. By controlling the dep-

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osition temperature, different microstructures were obtained. Study of the nanoindentation process of these films was conducted and the elastic modulus and hardness were determined. Using imaging equipment, the indentation crack was observed and the fracture toughness of films was estimated. Finally, the relationship between the microstructure and the mechanical properties was discussed.

2. Analysis

In the analysis of nanoindentation on a film structure, the effect of the substrate becomes important because the film thickness is comparable to the indentation penetration depth. Some semi-empirical relationships have been proposed, basically using variations of the rule of mixture in combination with experimental or finite element analyses. Deconvolution of the film properties from measurements of the composite film/substrate was a final goal. Recently, Jung proposed a simple equation for determining the elastic modulus and hardness properties of thin films on a substrate from nanoindentation experiments. An empirical formulation relates the modulus E and hardness H of the film/substrate to corresponding material properties of the constituent materials via a power law relationship. Geometrical dependence of E and H is wholly contained in the power law exponents, expressed in an inverted form to enable deconvolution of the film properties from data on the film/substrate. In the present study, Jung's method to analyze the hardness and the modulus of the films was used. It will be summarized in brief.[13]

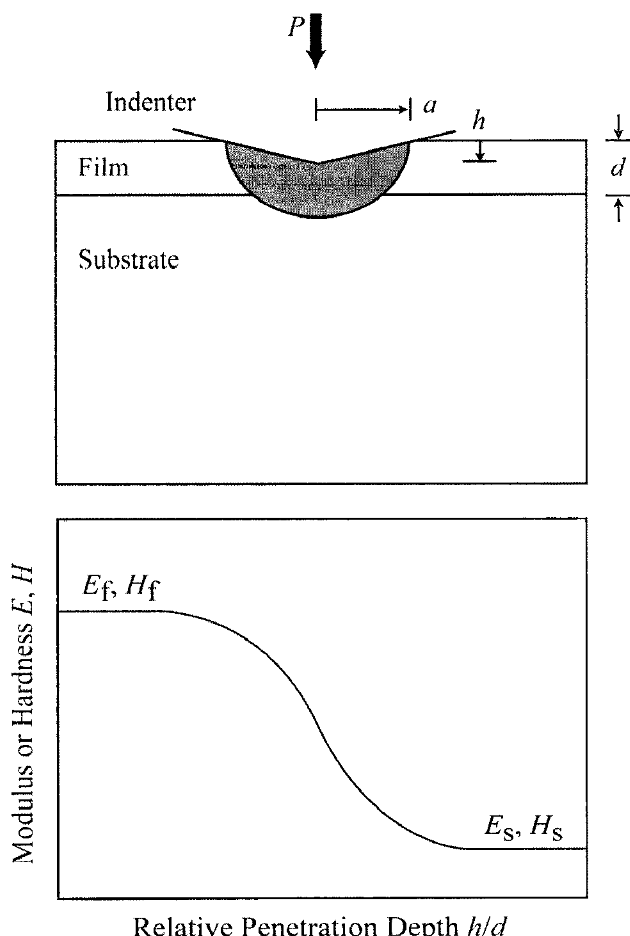

Fig. 1. Schematic illustration of fixed profile nanoindentation on a film/substrate structure including the hemisphere of influence for the deformation field and the simple power law curve for the film/substrate system.

Fig. 1 shows the film/substrate indentation system, consisting of an isotropic film of thickness d on a homogeneous substrate. A sharp indenter is pressed onto the top surface at load P, with a characteristic contact radius a at full contact, or, equivalently, a maximum penetration depth h. The elastic and plastic response will then change progressively from film-dominated at small a/d ratios to substrate-dominated at large a/d ratios with the transition centered around $a/d \sim 1$ and $h/d \sim 1/7$ for Berkovich and Vickers indenters, respectively. Accordingly, a simple approach previously used by H is adapted for spherical indentations by writing ratios modulus and hardness as power law functions as follows:

$$E = E_s(E_f/E_s)^L \quad (1a)$$

$$H = H_s(H_f/H_s)^M \quad (1b)$$

Here, the exponent terms are the dimensionless spatial function $L = L(h/d)$ and $M = (h/d)$. This formulation conveniently separates material and geometry terms. Eq. 1 must satisfy the essential boundary conditions $h/d = 0$, $E = E_f$ and $H = H_f$ (film-dominated), as well as $h/d = 1$, $E = E_s$, $H = H_s$ (substrate-dominated). These boundary conditions are the most simply and smoothly satisfied sigmoidal functions.

$$L = 1/[1 + A(h/d)^C] \quad (2a)$$

$$M = 1/[1 + B(h/d)^D] \quad (2b)$$

where A, B, C, and D are adjustable coefficients. Eq. 1 and 2 were used to measure the E and H values for chemical vapor deposited silicon carbide film on a graphite substrate.[18]

Nanoindentation provides a simple route for the evaluation of the fracture toughness. Sharp indenters are usually favored because the test can be carried out on routine hardness testing experiment. Lawn, Evans, and Marshall formulated a relationship in which they investigated a fully formed median/radial crack. They found that the ratio of the load and the crack size is a constant. In 1987, Laugier undertook an extensive review of previously reported experiments and determined a different formulation. Although the vast majority of toughness determinations using indentation techniques are performed with a Vickers diamond pyramid indenter, the Berkovich indenter has particular usefulness in nanoindentation work. However, the loss of symmetry presents some problems in determining the toughness of a specimen because half-penny cracks can no longer join two corners of the indentation. As proposed by Dukino and Swain, the modification has relevance to the crack pattern observed from indentations with a Berkovich

indenter. The Laugier expression can thus be written as

$$K_c = 1.073 x_v (a/l)^{1/2} (E/H)^{2/3} P/c^{3/2} \quad (3)$$

where x_v is 0.015, a is the impression size, l is the crack size from the impression edge, and c is the crack size. Attention is given to the length of the radial cracks as measured from the center of the indentation and the fracture toughness as determined by Eq. 3.[19,20]

3. Experimental Procedure

3.1. Sample Preparation

The deposition experiments were performed in a conventional hot-wall type horizontal double-tube type reactor. The peak temperature was measured at an approximate distance of 15 cm from the tube inlet. Methyltrichlorosilane (MTS, CH_3SiCl) was used as a precursor for depositing silicon carbide on isotropic graphite because its equivalent ratio of Si to C results in easy deposition on stoichiometric films. Hydrogen was used as a carrier gas, which transfers source precursor through the bubbler to reactor. Hydrogen was simultaneously used as a carrier gas and a dilution gas. The flow rates of the MTS and H_2 were 100 and 1000 sccm, respectively. The deposition process was carried out at temperatures of 1300 and 1350°C under a total pressure of 1.3 kPa for 2 h.

The microstructures of the silicon carbide coatings were investigated using a scanning electron microscope. The top surface was obtained as fabricated and a cross-section of the coating was prepared by cutting the specimen. The secondary electron mode was used for the observation of the grain shape, size, and distribution, and the backscattered electron mode was used to measure the indentation crack size. An X-ray diffraction method was used to investigate the crystallography of the silicon carbide coatings.

3.2. Nanoindentation

Two grades of chemical vapor deposited silicon carbide coatings were used in this study. Chemical vapor deposited coatings are fabricated with a fixed deposition; therefore, the thickness of the coatings was fixed. In order to adapt the E and H method, various specimens of different thicknesses were required. Simply, the coating specimen was mounted in acrylic resin with a tilting angle of 15° to the top surface, and the top surface was then ground with a diamond pad and polished with diamond slurry. A schematic illustration of the specimen preparation procedure is shown in Fig. 2. The tilt-grinded specimens were mounted on a nanoindentation system (Nanotest, MicroMaterials, UK). A nanoindentation was made on the film surface and on the polished region using a Berkovich indenter. Measurements were also made directly on a graphite substrate surface. Determinations of the values of E and H of the specimens were made from load-displacement curves over a range of indenter depth h of 100 to 400 nm. The Poisson's ratio of $\nu = 0.22$ was used for all materials in the modulus calculations. After the

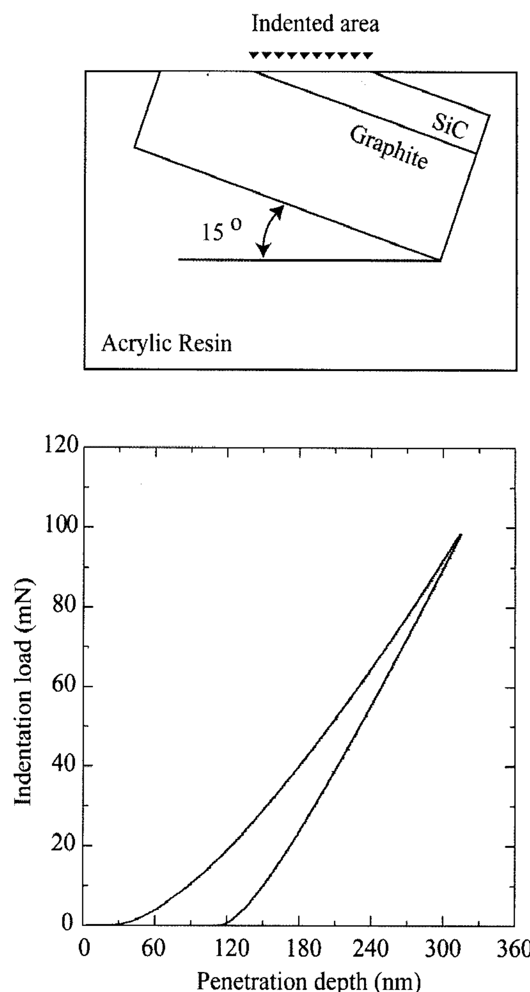

Fig. 2. Schematic illustration of a tilt-grinded specimen for nanoindentation experiments and the nanoindentation load-penetration curve.

indentation experiments, the specimen was sectioned to measure its precise thickness. The conventional load-penetration depth curve is shown in Fig. 2.

4. Results and Discussion

4.1. Microstructure

The effect of the temperature on the surface morphology of silicon carbide is shown in Fig. 3. Scanning electron microscopy of the as-deposited surface revealed a change from rounded hillocks to a faceted structure and then to well-developed crystals as the temperature increased. Under lower deposition temperatures, atoms are expected to have limited surface reactions on the substrate. This promotes continuous nucleation of new crystals growth sites and, thus forms smooth non-faceted structures. An examination of the faceted crystals shows that they contain many clear twin configurations and reentrant corners. These features indicate that a reentrant twin plays an important role in the growth of the silicon carbide in a chemical vapor deposition process. It is seen in Fig. 3 that the apparent grain size increases with the deposition temperature. The frac-

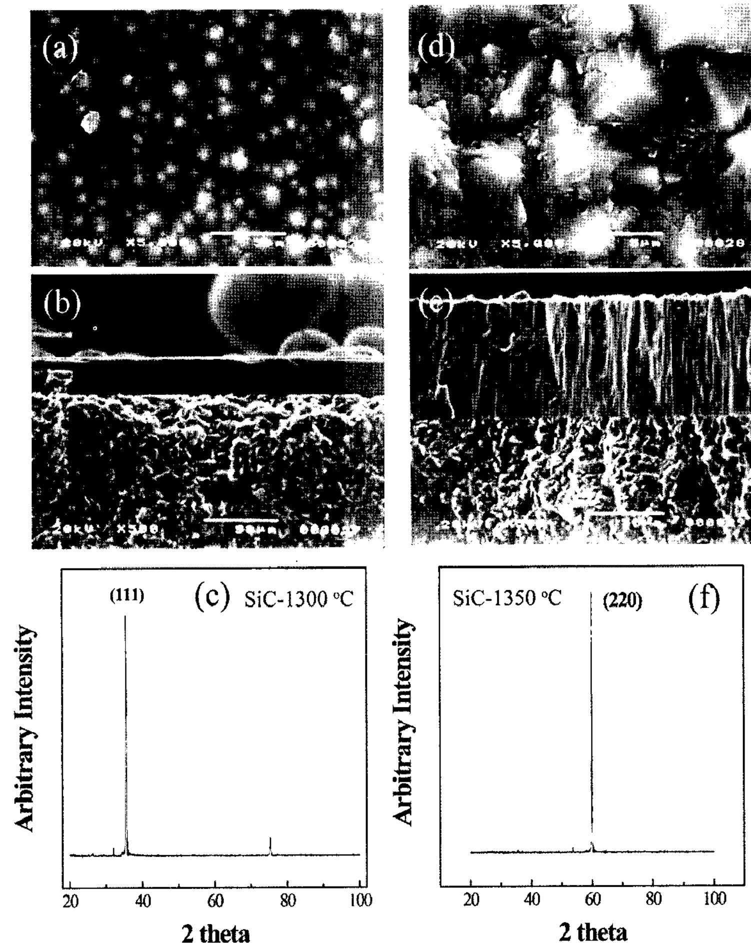

Fig. 3. Scanning electron micrographs of the surface layers of silicon carbide films on a graphite substrate, (a) top view (b) side view at a deposition temperature of 1300°C (e) top view, (f) side view at a deposition temperature of 1350°C, and X-ray diffraction pattern 2-theta scan of the silicon carbide films in (c) and (f).

ture surface of the coating layers observed by the scanning electron microscope is shown in Fig. 3. With silicon carbide deposited at 1300°C, the microstructure showed an isotropic morphology, whereas with silicon carbide deposited at 1350 °C, a clear columnar microstructure was observed.

Fig. 3 also contains the X-ray diffraction pattern of silicon carbide films deposited at 1300 and 1350°C. Silicon carbide films exhibited a strong preferred orientation of cubic SiC. At a lower deposition temperature and a higher growth rate, the surface-controlled reaction process dominated and the preferred orientation was (111). At a higher deposition temperature and higher deposition rate, the preferred orientation occurred on the less densely populated atomic planes or on higher surface energy lattice planes parallel to the surface, such as (220). The deposition model was proposed by Komiyama, and the results were in a good agreement with the proposed model.

4.2. Nanoindentation study

A nanoindentation was made on both silicon carbide specimens with an increasing maximum indentation load. As the indentation load increased, the modulus and hardness of the silicon carbide showed decreasing values. The indentation size effect, the compliant substrate, and the non-uniformity of the film may explain why the modulus and hardness decreased as the indentation load increased. In the small penetration depth experiments, the surface roughness and the tip roundness can affect the scattering of data. Hardness and modulus values were approaching their original values as the indentation load increased. There is a problem in determining the hardness and the modulus of silicon carbide films. Therefore, a tilt-grinded specimen was adopted to obtain the intrinsic properties of the film.

An indentation experiment was performed on the silicon carbide film of tilt-grinded specimens of different thicknesses. Two different indentation loads were applied and the hardness and the modulus were routinely determined by applying the Oliver-Pharr method to load-penetration curves. In order to extract the modulus and the hardness of a tilt-grinded silicon carbide specimen, the results were plotted as a function of the relative penetration depth, as shown in Fig. 4. At each end of the data range, as h/d becomes small, the modulus and hardness tend to shift upward for SiC films. As h/d becomes large, the modulus and hardness tend to shift downward to the graphite substrate. Solid curves through the data points are regression

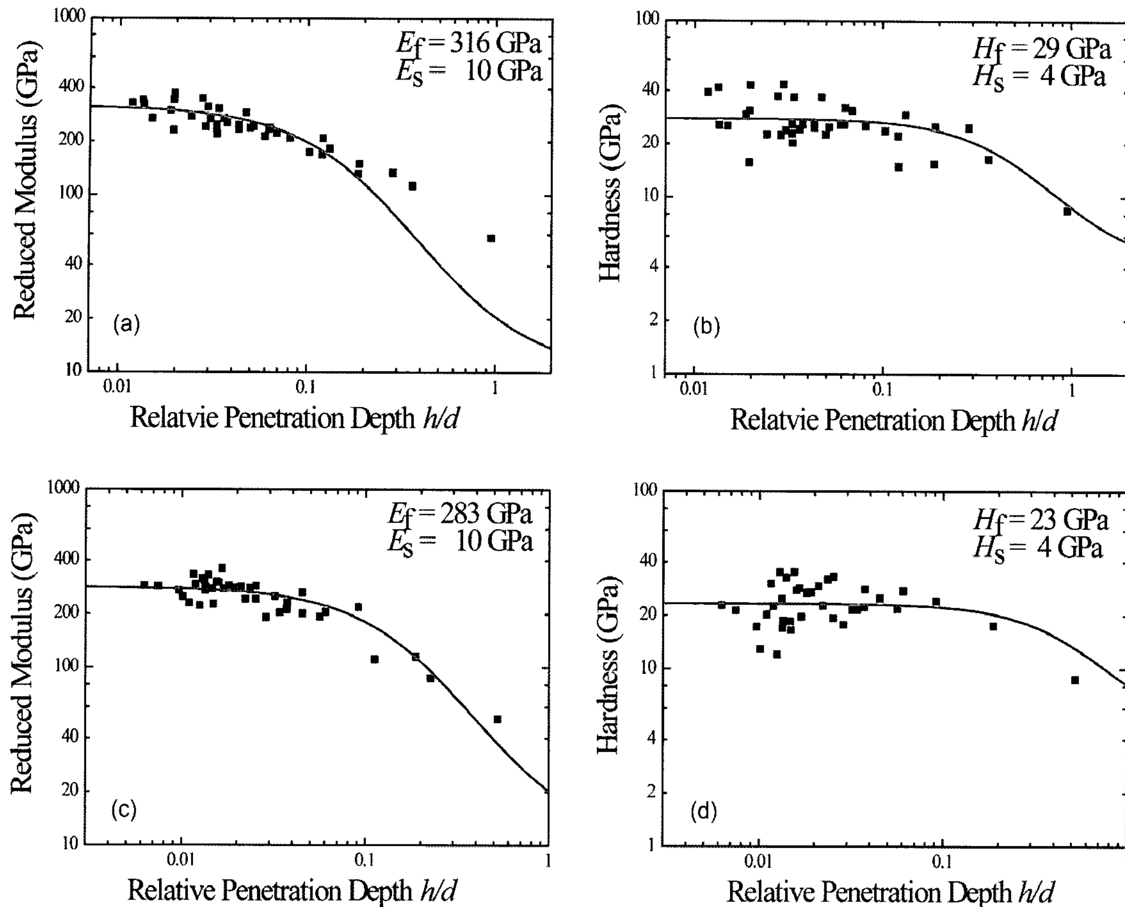

Fig. 4. Plots of the silicon carbide modulus and hardness as a function of the relative penetration depth h/d. Solid curves through the data are the best fits to the modulus and hardness equations. (a) modulus and (b) hardness for 1300°C silicon carbide and (c) modulus and (d) hardness for 1350°C silicon carbide.

fits to power law functions and yield E=316 GPa and H=29 GPa for silicon carbide deposited at 1300°C.

In the case of silicon carbide deposited at 1350°C, the same procedure was applied, as shown in Fig. 4. Curve fitting to the data yields relatively the low values E=283 GPa and H=23 GPa. The difference is believed to be due to the change of the preferred orientation and the microstructure. It was reported that the Vickers hardness on SiC with the (111) orientation was higher than that with the (200) orientation; the anisotropy was attributed to the active slip system of the cubic silicon carbide. In addition, the mechanical properties depend on the grain size and microstructure. It has been commonly accepted that hardness generally increases as the grain size decreases, and that a columnar microstructure has lower hardness compared to a domed-top grain structure. Therefore, it can be expected that the mechanical properties depend on the microstructure and that the SiC deposited at 1300°C has a higher modulus and hardness than that of silicon carbide deposited at 1350°C.

A nanoindentation experiment can be used to evaluate the facture toughness of films. An indentation load induces the plastic deformation of materials and a permanent plastic deformation zone creates additional residual stress. A crack is not generated below a critical load; hence, a high indenta-

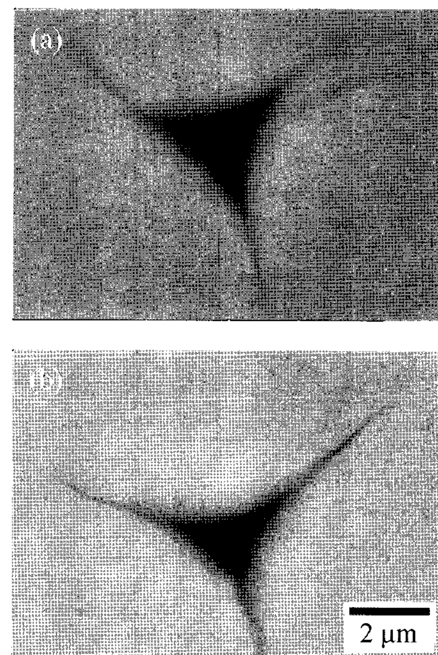

Fig. 5. Scanning electron micrographs of a Berkovich nanoindented area of silicon carbide on a graphite substrate, (a) at a deposition temperature of 1300°C and (b) at a deposition temperature of 1350°C.

tion load of approximately 200 mN was used. After the high load indentation, the indented area was observed using the scanning electron microscope, as shown in Fig. 5. Plastic deformation is apparent; however, the crack is not clearly shown. The crack is clearly shown in backscattered electron mode, however, and the crack size was measured for each specimen. The fracture toughness for each specimen was determined as K_c=9.8±2.4 for silicon carbide deposited 1300°C with K_c=6.1±1.6 MPa m$^{1/2}$. Care must be taken with the facture toughness because the absolute value of fracture toughness exceeds the fracture toughness of conventional silicon carbide, despite the fact that silicon carbide film is more brittle. It is difficult to consider absolute values as an exact material property. The fracture toughness values can be accepted merely as a relative comparison. It remains valid that a low-temperature specimen has greater fracture toughness compared to a high-temperature specimen.

5. Conclusions

Silicon carbide films on graphite substrates were fabricated by chemical vapor deposition. Two grades of silicon carbide were fabricated by changing the deposition temperature. The silicon carbide with a low deposition temperature has a smaller gain size and a domed-top isotropic microstructure, whereas the silicon carbide with a high deposition temperature has a larger grain size and a faceted columnar microstructure. The elastic modulus and hardness of the silicon carbide films were estimated using nanoindentation experiments on tilt-grind specimens. Additionally, scanning electron microscopy was used to measure the indentation crack size, and the fracture toughness of the films was determined. In conclusion, silicon carbide deposited at 1300°C is mechanically more stable than silicon carbide deposited at 1350°C due to its grain size, grain shape, and preferred orientation.

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