STRENGTH AND ELASTIC MODULUS OF NEUTRON-IRRADIATED CUBIC SILICON CARBIDE—Y. Katoh and L. L. Snead (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this task is to determine the influences of neutron irradiation on fracture strength parameters, including apparent strength, indentation hardness, fracture toughness and elastic modulus, of high-purity chemically vapor-deposited cubic silicon carbide.

SUMMARY

Mechanical properties of high purity polycrystalline cubic silicon carbide were characterized after neutron irradiation. The materials were irradiated in target position capsules in High Flux Isotope Reactor to nominal neutron fluence levels of up to 7.7 dpa at temperatures of 300, 500 and 800°C. Reduction in Young's modulus was observed after irradiation, and its irradiation temperature dependence agreed qualitatively with calculated modulus change due to point defect swelling. Irradiation caused very significant modification of statistical flexural strength but caused only minor increase in nano-indentation hardness. It was pointed out that the irradiation effect on fracture initiation through an enhanced cleavage resistance in large grains could be contributing to the major change in flexural strength properties.

PROGRESS AND STATUS

Introduction

Cubic silicon carbide (SiC), or beta-phase of SiC, is the primary constituent of advanced SiC fiber-reinforced SiC-matrix ceramic composites (SiC/SiC composites) which are considered for use in fusion blanket/first wall structures [1] and other advanced gas-cooled nuclear reactors [2]. For example, both the matrices and the reinforcing fibers comprise of polycrystalline cubic SiC in so-called advanced fiber CVI (chemically vapor-infiltrated) SiC/SiC composites, which are reference materials for fusion- and nuclear-grade SiC-based composites [1]. Matrices of these composites are essentially chemically vapor deposited (CVD) cubic SiC, since the CVI process for matrix densification is in principle a low temperature (deposition temperature of 950 ~ 1200°C) CVD of SiC on fiber surfaces as the substrates [3]. The matrix of developmental NITE (nano-infiltration and transient eutectic-phase process) SiC/SiC composite is primarily cubic SiC, because the matrix phase is liquid phase-sintered SiC reprecipitated at below 1800°C [4]. The advanced near-stoichiometric SiC fibers also consist of cubic SiC crystal grains along with a few mass percents of excess carbon, which presents as graphitic pockets at multi-junctions of SiC grains. Such fibers are represented by Tyranno™-SA (Ube Industries, Ltd., Ube, Japan) [5] and Hi-Nicalon™ Type-S (Nippon Carbon Company, Tokyo, Japan) [6], both commercially available.

SiC has long been proposed for use in coated fuel particles for gas-cooled thermal reactors. In the TRISO coating system [7], the SiC layer provides primary ability to contain the high pressure generated in the kernel regions by nuclear fission. In the standard TRISO coating condition at Oak Ridge National Laboratory, SiC-CVD in a fluidized bed at a deposition temperature of ~ 1500°C produces cubic SiC with typical grain size of ~ 10 microns at the outside surface.

In all of the above-mentioned application, understanding the effect of neutron irradiation on mechanical properties of cubic SiC is of crucial importance. The matrix micro-cracking stress for SiC/SiC composites, which roughly corresponds to both static and dynamic fatigue limits [8], can be subject to irradiation effect through modification of fracture energy and elastic moduli of the composites' constituents [9]. Statistical fracture strength of monolithic SiC is directly relevant to statistical probability of coating failure for fuel particles [10]. Limited amount of data on irradiated fracture strength support that little or no strength degradation occurs in CVD-produced SiC during neutron irradiation [11-13]. However, some of the published data are contradictory [14], probably because of that the strength of brittle ceramics can be sensitively affected by irradiation behavior of very small amount of second phases and modification of

surface conditions during irradiation. Additionally, quality of data could have been sacrificed by the limitation in number and size of specimens accommodated in irradiation capsules, due to the inherently statistical nature of fracture behavior of ceramics and the limited applicability of conventional test techniques. Therefore, in the present work, the influences of irradiation at temperatures of 300–800°C on fracture strength parameters, including strength, hardness and elastic modulus, were evaluated exclusively for identical material.

Experimental Details

Material used was CVD-SiC produced by Rohm and Haas Advanced Materials Company (formerly Morton International, Woburn, Massachusetts, 'R&H' hereafter). The R&H CVD-SiC is a single-phase cubic SiC with manufacturer-claimed purity of > 99.9995%. Typical concentrations of trace element impurities are provided elsewhere [15]. The amount of nitrogen has not been published, although it can be the impurity with highest concentration. The crystal grains of CVD-SiC are highly elongated along the growth direction and have a bi-modal size distribution of large (10 ~ 50 um in column width) and small (typically 1 ~ several um) grains. Typical examples of optical micrographs of polished and etched cross-sections are found in reference [16]. The crystal grains are heavily faulted and have a preferred crystallographic orientation of <111> direction in parallel to the CVD-growth direction but randomly oriented in the normal plane. All the flexural specimens were machined so that the longitudinal directions are normal to the growth direction. Slight difference in average flexural strength for specimens with longitudinal directions parallel and normal to the growth direction has been reported for the identical material [17].

Neutron irradiation was carried out in the flux trap of the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL) for 8 operation cycles. The neutron fluence and temperatures were 6.0 x 10^{25} n/m^2 (E > 0.1 MeV) at 300 and 500°C and 7.7 x 10^{25} n/m^2 (E > 0.1 MeV) at 800°C. The target temperature was maintained within ±10°C of the designated temperature for the most time. A neutron fluence of 1 x 10^{25} n/m^2 (E > 0.1 MeV) will be assumed equivalent to 1 dpa in SiC hereafter.

Elastic modulus and hardness were evaluated by means of ultra-low load depth-sensing indentation, on diamond-finished surfaces, using Nano-Indenter™ XP (MTS Systems Corp., Minneapolis, Minnesota) equipped with a Berkovich diamond tip. Elastic modulus and hardness for individual indentation were obtained by averaging slightly depth-dependent indentation modulus and contact pressure measured in a continuous stiffness measurement (CSM) mode [18] over the contact depth range of 500–1000nm. Indentation was made at 20 different locations on each sample, which were randomly selected and separated at least 100 um each other.

Flexural test was performed using rectangular beam specimens with dimensions of 1 x 1 x 25 (width x height x length in millimeter) in a four point - 1/3 point configuration, defined in ASTM Standard C1341-00, with support/loading spans of 20/6.67 mm, respectively, and in otherwise following general guideline of ASTM Standard C1161-02C. Details of the flexural test procedure are found elsewhere [13]. Fracture origins were located by optical microscopy and the fracture surfaces were examined by scanning electron microscopy for selected specimens.

Results and Discussion

(1) Elastic Modulus

The dynamic nano-indentation elastic modulus profiles measured for samples irradiated at 300, 500 and 800°C are plotted in Fig. 1 (A) against contact depth after averaging. Unrealistically high apparent moduli at contact depth smaller than ~ 200nm approached to literature value of ~ 460GPa for unirradiated SiC at contact depth of 1000 nm. In all the measurements, elastic moduli seemed to be approaching to asymptotic values as the contact depth increased but never reached them at 1000 nm. Such behavior is believed to be related with the non-homothetic progressive crack extension during nano-indentation and

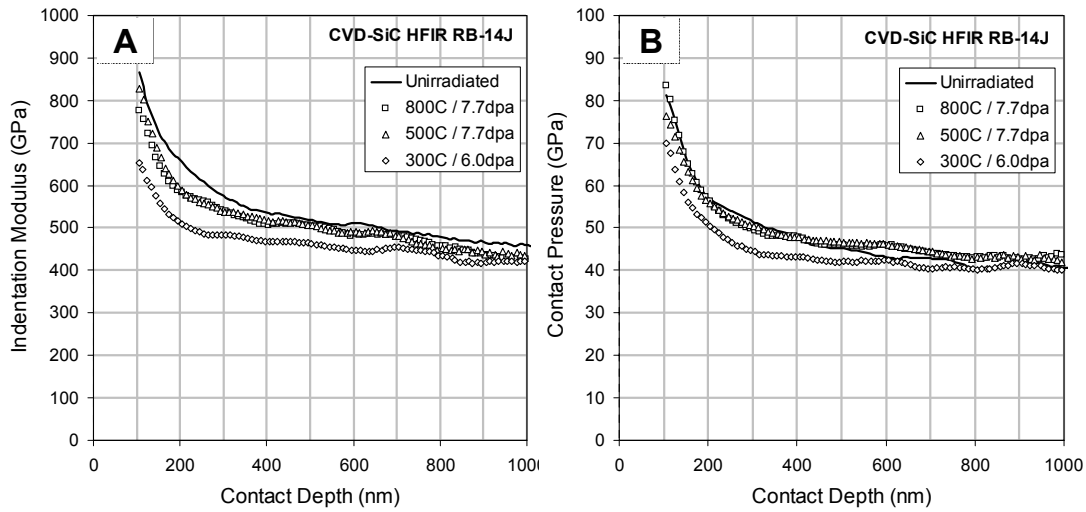

Fig. 1. Depth-profiles of Young's modulus-equivalent dynamic indentation modulus (A) and nano-indentation hardness (B) of unirradiated and irradiated CVD-SiC.

the influence of indenter tip shape. Park et al. reports that major median cracks are produced in CVD-SiC by nano-indentation with a Berkovich indenter before the contact depth reaches a few hundreds of nanometers [19].

The influence of neutron irradiation was not very significant but obvious. The measured nano-indentation properties are summarized in Table 1. Swelling data were added from reference [13]. The irradiation at 300°C caused the most significant modulus decrease, while the irradiation at 500 and 800°C resulted in similar and smaller modulus decrease. The difference between 500 and 800°C irradiation was not statistically significant, due probably to relatively large data scatter at 500°C for unknown reasons. Upon conversion of indentation modulus to Young's modulus, Poisson's ratio of 0.18 was assumed and the potential effect of irradiation on Poisson's ratio was not considered. The influence of minor modification in Poisson's ratio (ν) should be small, as the converted Young's modulus is proportional to ($1-\nu^2$) [18].

Table 1. Summary of nano-indentation properties

	Elastic Modulus (GPa)			Hardness (GPa)			Linear Swelling
	Average	Std Dev	% Change	Average	Std. Dev.	% Change	
Unirradiated	456.5	10.4	-	40.6	1.1	-	-
300C, 6.0dpa	416.6	11.9	- 8.7%	40.4	1.0	- 0.5%	0.67%
500C, 6.0dpa	428.5	19.6	- 6.1%	41.7	1.6	+ 2.7%	0.55%
800C, 7.7dpa	426.1	10.8	- 6.7%	42.6	1.4	+4.9%	0.27%

In Fig. 2, irradiation temperature dependence of Young's modulus change is plotted along with published data [11,12,20]. All the modulus data in Fig. 2 were taken by nano-indentation on R&H CVD-SiC samples irradiated to 0.15–7.7 dpa. Irradiation generally reduces modulus and the extent of reduction is more significant at a lower irradiation temperature. The modulus reduction becomes negligible when irradiation temperature reaches or exceeds ~ 1000°C. There seems to be an indistinct stage between 800 and 1000°C.

These features in the temperature dependency have been observed for 'point defect swelling' of SiC [21]. Point defect swelling is an isotropic volume expansion that is believed to occur by lattice relaxation due to

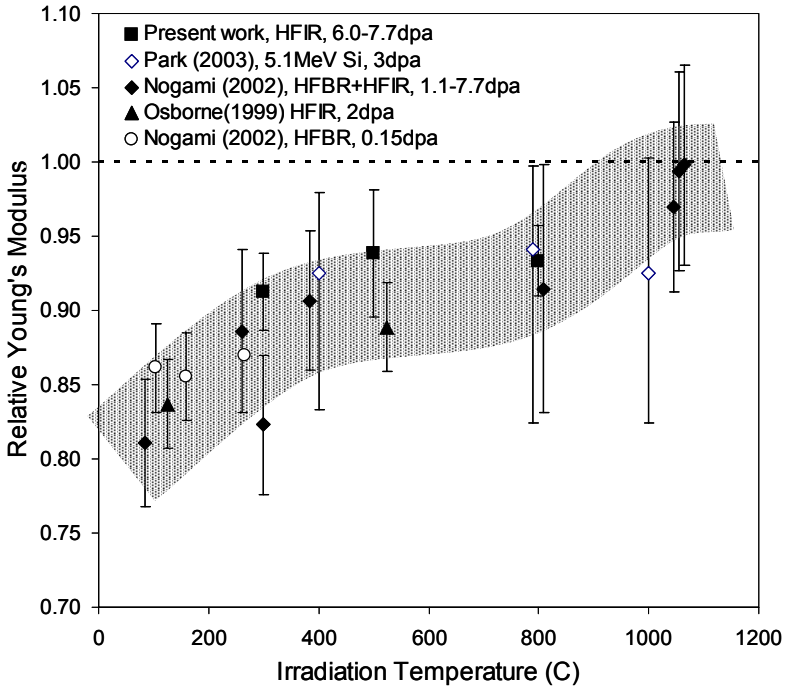

Fig. 2. Irradiation temperature dependence of irradiated Young's modulus of CVD-SiC, at ambient temperature, normalized to unirradiated values. The error bars are showing standard deviations for all the neutron data points and ranges of data scatter for the ion data points.

accumulated isolated point defects and small point defect clusters during irradiation at temperatures where vacancies are not readily mobile. In SiC which underwent point defect swelling, a very good agreement of dimensional expansion with lattice spacing has been confirmed by X-ray diffractometry studies [22].

An estimation of the influence of lattice relaxation on Young's modulus was attempted by a calculation using Tersoff potential [23]. The result predicted, as shown in Fig. 3, that linear lattice swelling of 1% causes approximately 10% reduction in Young's modulus. The predicted Young's modulus change could be varied up to tens of percents depending on a selection of interatomic potential, and Tersoff potential gives relatively high sensitivity of modulus to the interatomic distance. Therefore, measured elastic modulus changes observed in this experiment are generally greater than the theoretical prediction. Quantitative reliability of either the nano-indentation modulus or the potential function used is not sufficient for further discussion. Nonetheless, it could be concluded that the lattice expansion is a major cause of the irradiation-induced elastic modulus reduction in SiC.

Similar but more pronounced trend was observed in the irradiated flexural strength, for which the data are summarized in Table 2. Neutron irradiation at 300°C did not significantly alter the average flexural strength of CVD-SiC, while at 500 and 800°C strengthened by approximately 45–50%. Like other brittle ceramics, SiC is believed to obey the Griffith fracture criterion:

$$\sigma_f = \left(2E\gamma_0 / \pi c\right)^{1/2} \quad (1)$$

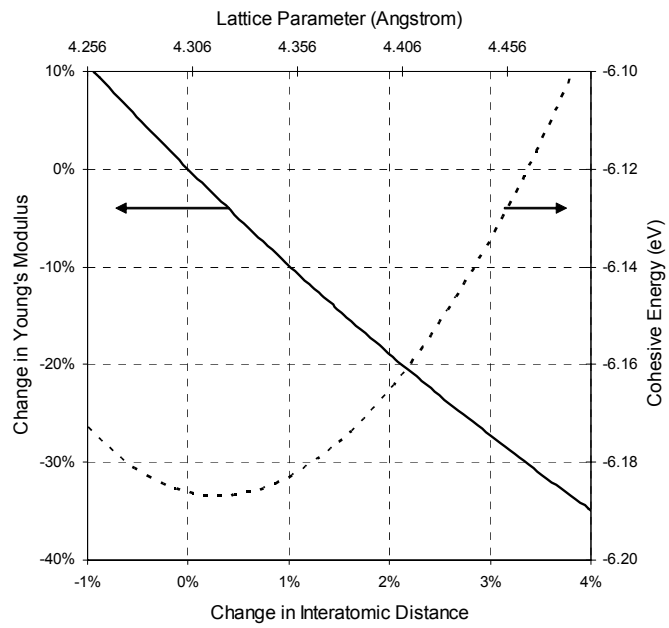

Fig. 3. The influences of interatomic distance change on Young's modulus and cohesive energy of 3C-SiC calculated using Tersoff potential. The cohesive energy is for average of SiC_4 and Si_4C unit tetrahedra.

Table 2. Summary of flexural strength properties

	Average Strength (MPa)	Std Dev (MPa)	% Change	Weibull Modulus	Number of Samples
Unirradiated	402	41	-	9.9	25
300C, 6.0dpa	419	85	+4	5.5	10
500C, 6.0dpa	606	66	+51	10.8	20
800C, 7.7dpa	578	85	+44	7.9	29

where σ_f is fracture stress, E is Young's modulus, γ_0 is effective fracture surface energy, and c is the crack length. According to Eq. (1) and data shown in Tables 1 and 2, neutron irradiation at 500 and 800°C apparently caused substantial increase of the fracture energy, while at 300°C it may have caused a minor increase of the fracture energy. On the other hand, for brittle ceramics, indentation hardness is generally observed to be proportional to the fracture stress, thus:

$$H = n\sigma_f \tag{2}$$

where n typically falls in a range of 20–50. This equation gives only a rough trend of common features for ceramics, but the relationship seems reasonable to some extent because both the indentation hardness and the averaged fracture stress are determined primarily by Mode-I fracture toughness. If we assume such a relationship, Eqs. (1) and (2) and data in Table 1 give 8–18% irradiation-induced fracture energy enhancement. In this case, the degree of enhancement is positively correlated with the irradiation temperature.

Present and published data regarding the irradiation effects on flexural strength, nano-indentation hardness, and indentation fracture toughness of R&H CVD-SiC in a fluence range of 0.15–18.7 dpa are compiled in Fig. 4. The general trend is that the irradiation-induced strengthening or toughening seems to be significant at 300–1000°C, in spite of the significant decrease in Young's modulus, which confirms the increase in fracture energy by irradiation.

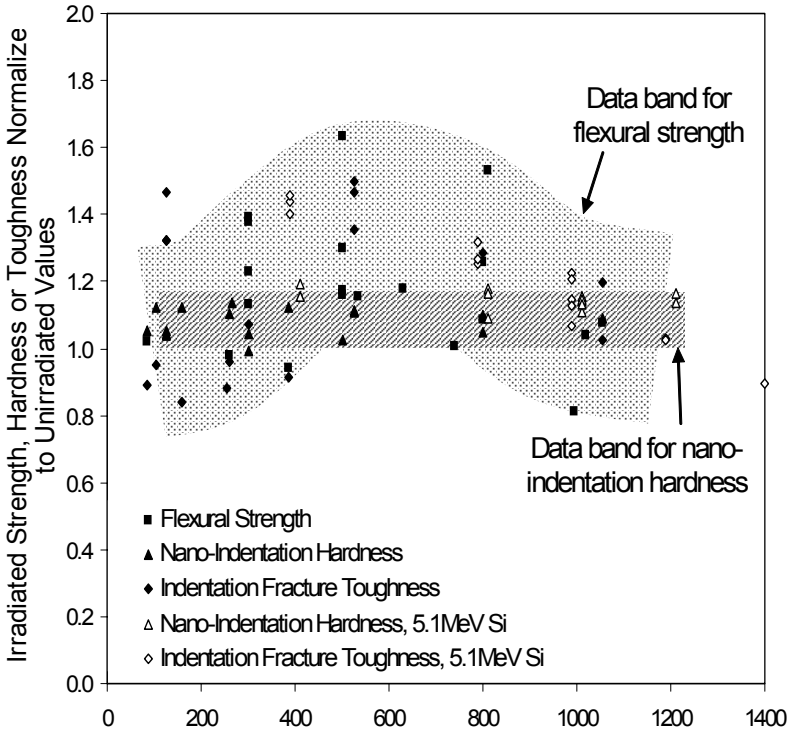

Fig. 4. Plots of fracture strength parameters (flexural strength, nano-indentation hardness and indentation fracture toughness) of CVD-SiC at ambient temperature as a function of irradiation temperature.

It is interesting to note that, in Fig. 4, the nano-indentation hardness exhibits relatively small and positive irradiation effect that is insensitive to the irradiation temperature. The width of data band for nano-indentation hardness is also small, as well as the individual data point represents a set of data which have a small scatter, too. This observation is contrasting to that both the flexural strength and the indentation fracture toughness data indicate a broad peak at an intermediate temperature while accompanying a large scatter.

The large scatter in flexural strength of brittle ceramics is inevitable, since the fracture strength is determined by the effective fracture toughness and morphology and characteristics of the flaw that caused the fracture. Irradiation possibly modifies both the flaw characteristics and the fracture toughness, through potential surface modification, relaxation of the machining-induced local stress, modifications of elastic properties and fracture energy. Because of such a complex nature of the apparent fracture strength, flexural strength measurement may not be an appropriate experimental technique for irradiation effect studies of ceramics for purposes other than engineering data generation. On the other hand, nano-indentation hardness is not affected by potential modification to the surfaces and surface features, because the indentation is usually performed to surfaces polished after irradiation. Nano-indentation hardness is determined primarily by the dynamic crack extension resistance mostly in bulk, though near

surface, and therefore should be more relevant to fracture toughness. The disadvantage is in that the irradiation effect can possibly be deemphasized due to the residual stress in subsurface introduced during polishing, in addition to the difficulty in relating the hardness with more commonly accepted strength parameters.

The scatter for indentation fracture toughness plots is caused probably by both the surface effect and the lack of standard experimental procedure. The indentation should be applied on sufficiently polished surfaces, but conditions of polishing are not always provided in literature [12,20]. Crack length measurement is done in either an optical microscope, a conventional SEM or a field emission SEM, all of which gives very different crack visibility. In addition, a few different models have been used for derivation of fracture toughness. As a conclusion, indentation fracture toughness measurement is an efficient technique for estimation of irradiation-induced toughness modifications, however, validation of the results requires very careful practice and flawless reporting of the experimental details.

(3) Statistical Strength and Fracture Surfaces

In Fig. 5, Weibull statistical plots of the flexural strength of unirradiated and irradiated samples are presented. By irradiation at 500 and 800°C, Weibull modulus slightly decreased and at the same time the fitted line shifted toward the higher fracture stress direction. The horizontal shift indicates a simple toughening, or an increase in fracture toughness alone [24]. After irradiation at 300°C, Weibull modulus reduction and slight embrittlement, or a decrease in fracture toughness, were observed.

Weibull modulus reduction for fracture strength due to neutron irradiation has been reported for various ceramics. Dienst tried to attribute it to the intrinsic nature of irradiation-produced defect structures, which substitute for the role of flaws responsible for unirradiated fracture, and flaw blunting by local stress

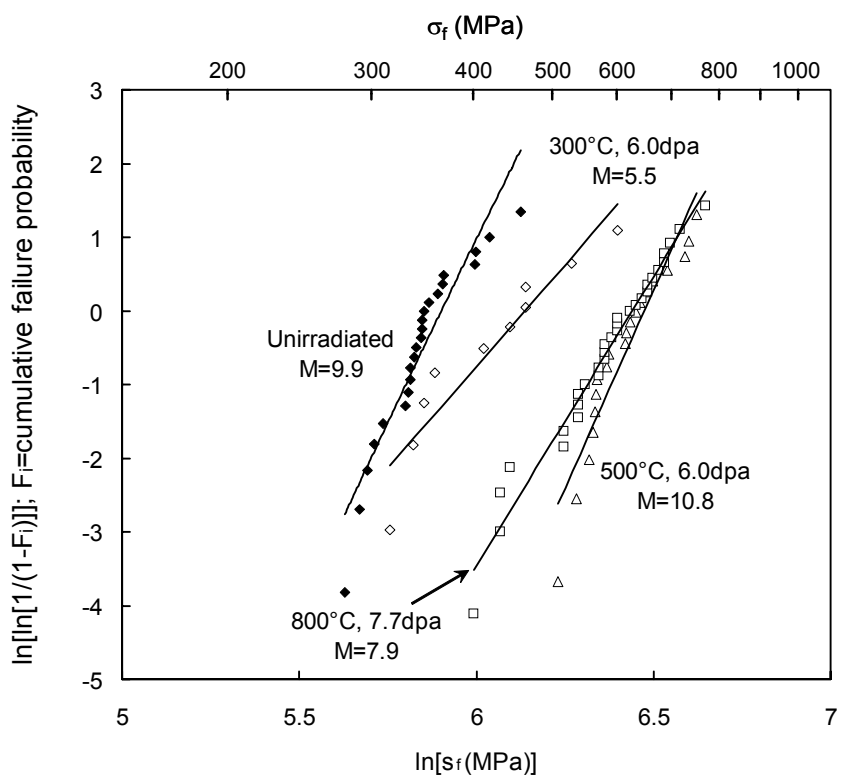

Fig. 5. Weibull plot of flexural strength of unirradiated and irradiated CVD-SiC.

relaxation in the high strength domain [14]. The former mechanism could not operate in the present case, because the irradiation produces homogeneously distributed nano-sized defect structures, while the typical flaw sizes which caused fracture in the present experiment are estimated to be 50 ~ 100um when semicircular surface flaw and KIc of ~ 3MPa-m-1/2 are assumed. The flaw blunting is a possible mechanism for the apparent toughening, however, further study is necessary to examine the flaw size-dependence of the blunting efficiency.

For the case of unirradiated CVD-SiC, fracture origin was always at or very close to surface on the tension side. Although the crack initiation site could not always be identified, in 12 of the 13 observed specimens, it was likely to be a combination of a large grain (or large grains) and a machining-induced surface flaw (1 specimen fractured from a large surface flaw). This interpretation is based on observation that the surface flaw found at the fracture origin itself was too small to explain the measured strength and cleavage of a large grain adjacent to the surface flaw was apparent, as shown in Figs. 6 (A) and (B). Fracture initiation at a large grain in R&H CVD-SiC is reported by Vern Cockeram [17]. It is also reported that Coors CVD-SiC, which is free from large grains, exhibits substantially higher fracture strength than

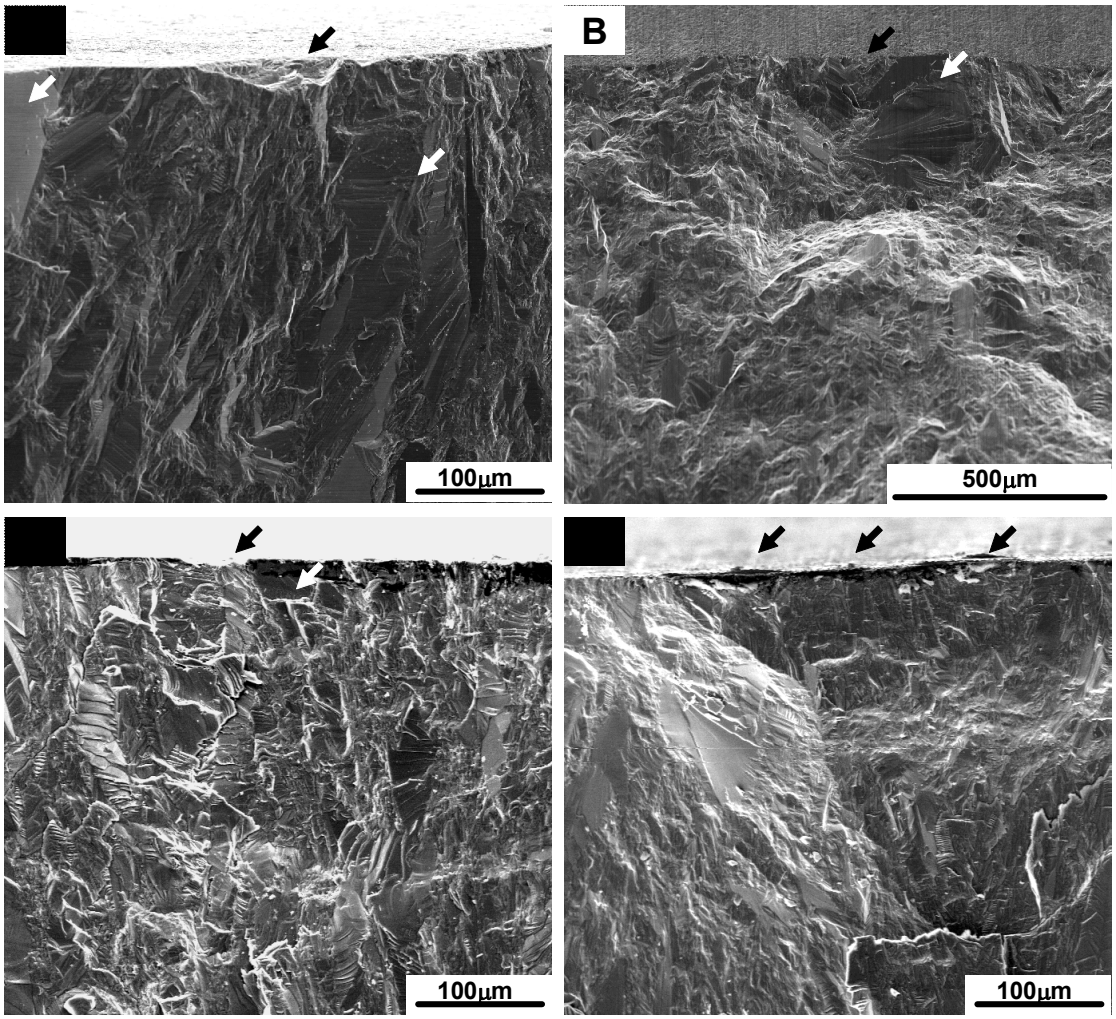

Fig. 6. Fracture origins of flexural tested CVD-SiC samples. (A) unirradiated, σ_f = 480MPa, (B) unirradiated, σ_f = 430MPa, (C) irradiated to 7.7dpa at 800°C, σ_f = 700MPa, and (D) irradiated to 7.7dpa at 800°C, σ_f = 480MPa. Surface flaws and large grains are indicated by arrows in black and white, respectively.

R&H CVD-SiC when machining condition is identical [17]. Clean and plain cleavage of large grains frequently observed in the fracture surfaces, as seen in Fig. 7 (A), indicates low fracture energy on preferred crystallographic planes in cubic SiC. Therefore, it is generally supported that the presence of large grains is influencing the strength of R&H CVD-SiC.

For the case of samples irradiated at 800°C, as shown in Fig. 7 (B), cleavage of large grains is not as marked as in unirradiated fracture surfaces. This is because the irradiated transgranular fracture of large grains did not leave surfaces as clean and plane as for the case of unirradiated grains, and hence indicating the increased transgranular fracture energy. It could contribute to increased resistance against both fracture initiation and crack propagation and thus increase fracture strength and indentation hardness. In Fig. 6 (C), which shows a fracture surface of the specimen exhibited high strength (σ_f = ~ 700MPa), the probable fracture origins are relatively small surface flaw and the adjacent large grain. In

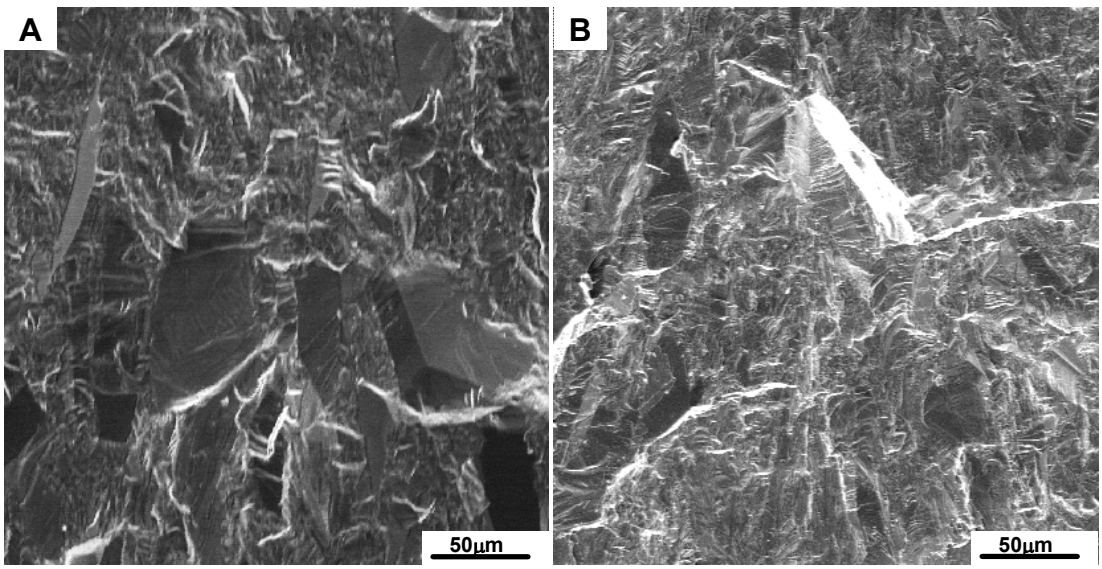

Fig. 7. Fracture surfaces showing the typical differences in cleavage surface fraction and appearance between unirradiated (A) and 800°C-irradiated specimens.

this case, fracture energy increase in the large grain should have increased the fracture stress significantly. On the other hand, when large flaw was nearly exclusively responsible for the fracture as shown if Fig. 6 (D) (σ_f = ~ 480MPa), the irradiation effect on fracture stress should have not been very significant. The Weibull modulus reduction by irradiation can thus be accounted by the reduced contribution of large grains when fracture strength is controlled by the combined effect of surface flaw and large grains.

Future Work

This work will be continued in order to better understand the effects on neutron irradiation on fundamental mechanical and physical properties of SiC. Young's modulus of neutron-irradiated CVD SiC will be determined with improved accuracy by impulse excitation and vibration method. Statistical fracture strength experiment will be carried out in near future irradiation opportunity. Determination of irradiated fracture toughness of CVD SiC is also planned employing dedicated notched beam specimens.

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