3.1 SWELLING AND X-RAY PEAK BROADENING OF HIGH DOSE NEUTRON IRRADIATED SiC COMPOSITES — C. Shih, R. Meisner, Y. Katoh, and L. L. Snead (Oak Ridge National Laboratory)

OBJECTIVE

The main objective of this work is to study the effect of high dose neutron irradiation on an early generation nuclear grade SiC/SiC composite, focusing on lattice parameter changes (using XRD techniques) and macroscopic dimensional changes following neutron irradiation up to ~70 dpa.

SUMMARY

The lattice parameter changes in high dose (up to ~70 dpa) neutron irradiated nuclear grade SiC/SiC composites were studied with room temperature powder XRD and compared with macroscopic dimensional changes at nominal irradiation temperatures of 300, 500 and 800°C. The results show no lattice parameter change for all high dose neutron irradiated SiC/SiC composites while macroscopic volume swelling is observed. This observation agrees with the very limited literature data on XRD studies of high dose CVD SiC and high dose hot pressed SiC. The lattice parameter changes disagree with macroscopic dimensional changes, suggesting progressive evolution of microstructures involving transition of ultra-fine interstitial clusters into larger interstitial loops as the very high irradiation doses are achieved. However, the errors in lattice parameter measurements caused by high surface roughness of the unpolished composites remains an issue and need to be further studied.

PROGRESS AND STATUS

Introduction

Nuclear grade SiC fiber reinforced SiC matrix (SiC/SiC) composites have excellent thermal, mechanical, and chemical stability with nuclear systems [1-3]. They also showed high radiation stability and low neutron activation; render them suitable for application in fission and fusion reactors. The thermal physical and mechanical properties of SiC/SiC composites have been studied intensively. Moreover, it is generally agreed that the “prove-of-principle” phase of nuclear grade SiC/SiC composites development has been finished and the R&D on SiC/SiC composites is shifting to the more pragmatic phase [4]. However, there is a lack of experimental data on the effect of high dose (>20 dpa, displacement per atom) irradiation partly because the lack of affordable neutron sources. Since the core materials in a fusion reactor is expected to suffer radiation damage of hundreds of dpa, it is critically important to study the effect of high dose irradiation on those candidate materials.

In this report, x-ray diffraction (XRD) analysis with Bragg-Brentano geometry was used to study the phase composition and lattice parameter changes in nuclear grade SiC/SiC composites upon neutron irradiation to fluences of up to ~70 dpa at irradiation temperatures of 300, 500 and 800°C. The results are compared with the measured macroscopic length changes. Some other property changes of the same composites under the same irradiation campaign can be found if ref [1].

Experimental

The composite material studied was two-dimensional (2D) 5-harness satin-weave Hi-Nicalon™ Type-S SiC fiber reinforced chemically vapor-infiltrated SiC matrix composites (HNLS composite). The HNLS composite was fabricated by Hyper-Therm High Temperature Composites, Inc. (Huntington Beach, CA) using the isothermal chemical vapor infiltration (I-CVI) method with multilayer fiber coating of pyrocarbon (PyC) and SiC. In the multilayer PyC/SiC interphase, the first SiC layer of 100 nm thick was deposited following the deposition of a thin PyC layer of 20 nm directly onto the fiber surface. Then, three SiC/PyC bi-layers were deposited, followed by the CVI SiC matrix deposition. Transmission electron microscopy images of the non-irradiated multilayered interphase structure and the selected area diffraction patterns showing the polycrystalline beta-phase SiC as the dominant phases in all the constituents, namely the fiber, interphase, and matrices, are presented in Fig. 1 [3].

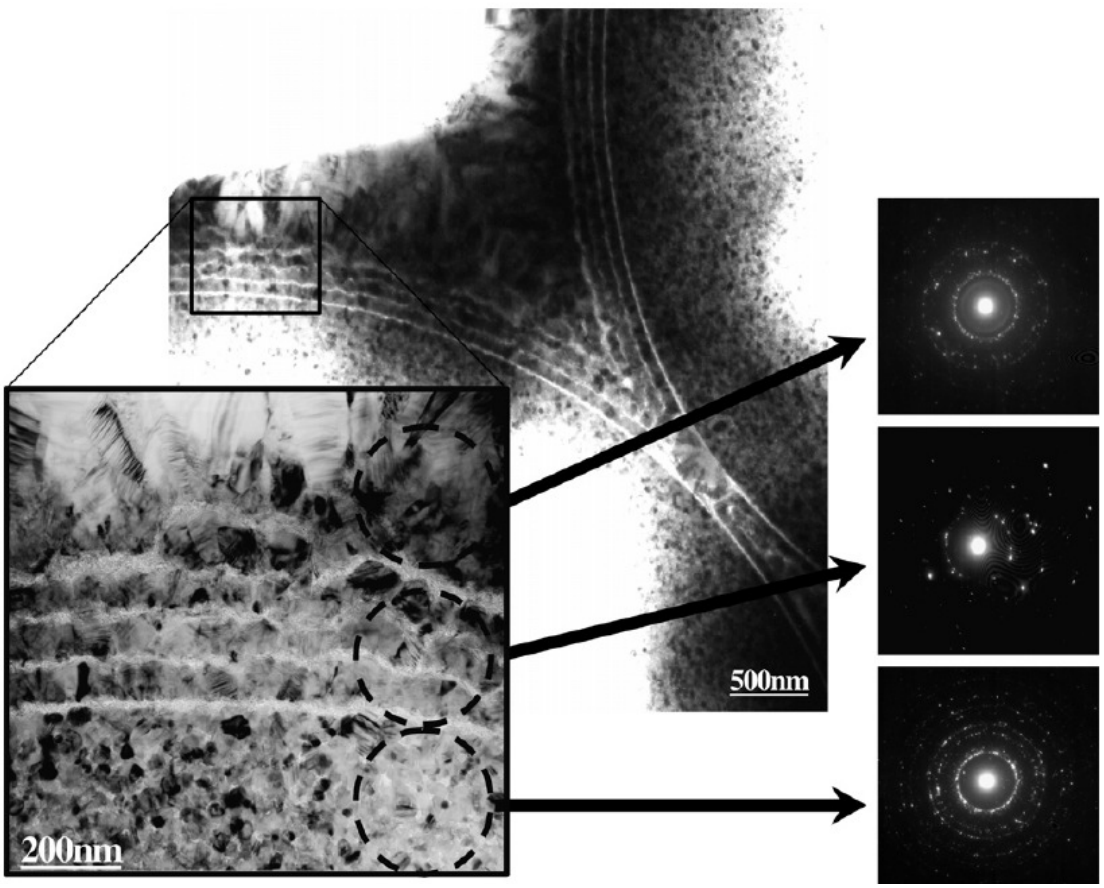

Fig. 1. TEM images of multilayer interphase of SiC/SiC composites [3].

The HNLS composites were machined into rectangular bars of various sizes and were irradiated in HFIR at ORNL using the flux trap fixed rabbit tube facility with a fast neutron flux of ~1 × 10^{19} n/m^2/s (E > 0.1 MeV). Photographs of a typical rabbit capsule before assembly and the HNLS composite samples are shown in Fig. 2. The samples were irradiated to neutron fluences of ~28 dpa (irradiation temperature of 300°C (27.8 dpa), 500°C (28.2 dpa), and 800°C (28 dpa)), 40.7 dpa (irradiation temperature of 800 °C) and ~70 dpa (irradiation temperature of 300°C 71

dpa), 500°C (74 dpa), and 800°C (71 dpa)); 1 dpa equals 10^{25} n/m^2 (E>0.1 MeV) is assumed throughout this report. The irradiation temperature was determined by post-irradiation annealing of room temperature electrical resistivity of dedicated CVD SiC thermometry samples, which had been irradiated in contact with the rectangular HNLS composites samples [5].

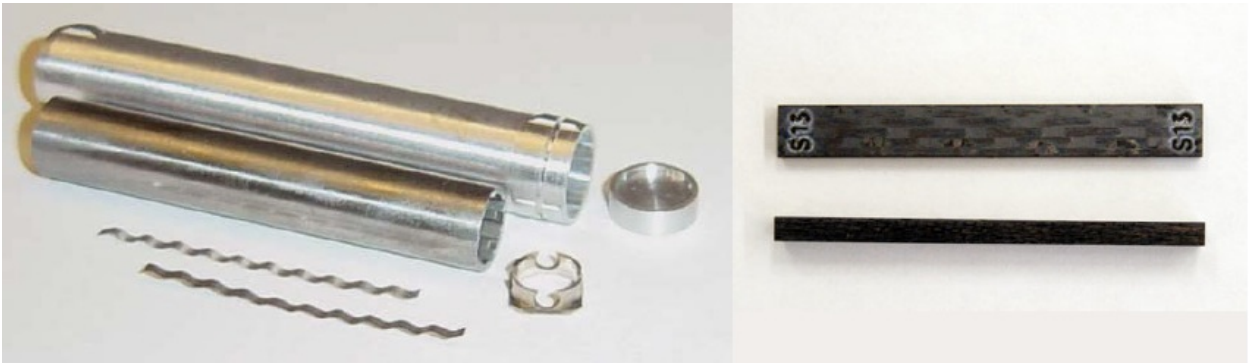

Fig. 2. HFIR rabbit capsules before assembly (left: capsule housing, specimen holder, and springs are shown on top, middle, and bottom, respectively, and capsule end cap and centering thimble are shown on right) and a pair of HNLS composite samples. Length of specimens and specimen holder are about 5 mm.

Following irradiation, the dimensions of the samples were measured using a caliper to an accuracy of 10 μm. The length change of the rectangular bars was used to calculate the macroscopic volume change of the samples, with the assumption that sample irradiation swelling is isotropic. For the lattice space change study with XRD, continuous θ-2θ scans were performed on the Panalytical X'pert diffractometer (Westborough, MA) from nominally 5° to 110° 2θ angels in 60-minute scans using CuKα radiation (λ=1.540598 Å) and the X'Celerator detector. All scans used ¼° fixed slits and ½° anti-scatter slit. The height of the sample was adjusted using the (111) peak of Moissanite-3C (β-SiC) with the sample placed on a zero background plate with a Kapton™ film. A search match was conducted using the "Jade" and/or "HighScore" software and the ICDD database. Power XRD was also conducted on non-irradiated HNLS composite, CVD SiC (Dow Chemical, Marlborough, MA), and bare Hi-Nicalon™ Type-S SiC fibers as reference materials. In order to accurately determine the lattice parameters, Si power was sprinkled on top of the specimens as an internal standard for all the XRD studies except for ~70 dpa irradiated SiC/SiC composites and un-irradiated bare SiC fibers.

Results and Discussion

<u>XRD profiles of non-irradiated samples</u>

The XRD profiles of non-irradiated samples, including Hi-Nicalon Type S (HNLS) bare fibers, CVD SiC, and HNLS composites (with and without Si powder) are shown in Fig. 3. Only 3C-SiC (β-SiC) phase is identified in CVD SiC and HNLS bare fibers. One unique character for the profile of HNLS fibers is the obvious shoulder on the low angle side of the (111) peak near 36° 2θ angle. The XRD profiles of HNLS bare fibers appear to be indistinguishable from the work by Gosset *et al*. on the same fibers [6], validating that the XRD diffractometer worked correctly. The HNLS fiber XRD profile suggests that the fibers contain a high density of planer defects, such as stacking faults. CVD SiC showed narrower peak width, suggesting less planer defects than HNLS fiber. The HNLS composites profiles show both β (3C) and α (2H) polytypes of SiC. Since the α peaks were not observed for HNLS fibers heat treated up to

1900°C [6]. The α (2H) peaks from the HNLS composites are likely form the CVI SiC matrix.

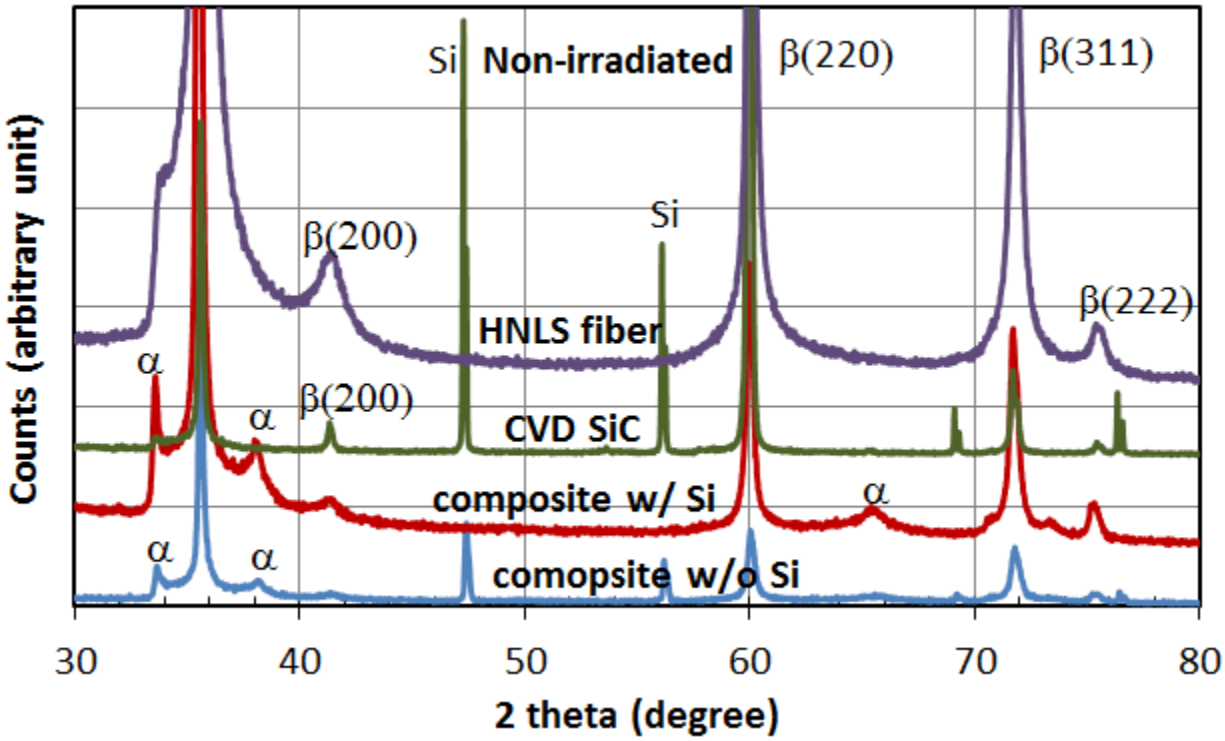

Fig. 3. XRD profiles of non-irradiated samples, including Hi-Nicalon Type S bare fiber, CVD SiC, and HNLS composites with and without Si powder.

Neutron irradiated HNLS composites

The ~28 dpa and ~70 dpa irradiated HNLS SiC/SiC composites XRD profiles are shown in Fig. 4 and Fig. 5, respectively, with un-irradiated composite profile as a reference. Because of the complex structure of the woven composites and the inherent high stacking fault density of both fiber and matrix in the composites [6,7], rigorous analysis of the XRD profiles are not feasible. XRD peaks from both 3C-SiC (β type) and 2H-SiC (α type) polymorphs are identified and are labeled in Fig. 4 and Fig. 5. The high stacking faults in the composites likely contribute to the 2H-SiC peaks. No new phases were detected by the XRD techniques following irradiation. The insert in Fig. 4 shows the details of the 35.6° peaks for ~28 dpa irradiated composites. The higher peak intensity of the 300°C irradiated composites is caused by larger sample size. It can be clearly seen from the insert that the non-irradiated composite has the smallest full peak width at half maximum (FWHM). The irradiated composites showed increased FWHM, caused likely by radiation-induced defects and associated lattice micro strains. A general observation is that peak broadening on the ~35.6 peak is larger for the lower temperature irradiated composites. This indicates that defect caused lattice strain might contribute to the observed peak broadening. However, no conclusion could be drawn from the Williamson-Hall analysis because the peak broadening is inconsistent along 2θ angels, causing very poor linearity. This behavior is likely caused by high density of certain type of defects, leading to line broaden of certain peaks [6]. A more rigorous analysis is ongoing and will be discussed in future reports.

The lattice constant (d space) of SiC, calculated with the software using Si powder as an

internal standard (except ~70 dpa irradiated samples, which did not have internal standard) is presented in Table 1. The d space value for non-irradiated HNLS composites with Si power is used as a reference to calculate the percent lattice constant change of all the irradiated composites. The macroscopic length changes for the same samples are also presented. Some historical data of CVD SiC high dose neutron irradiation studies are included in Table 1. To the authors' best knowledge, no data are available for XRD profiles of neutron irradiated SiC/SiC composites in the open literature.

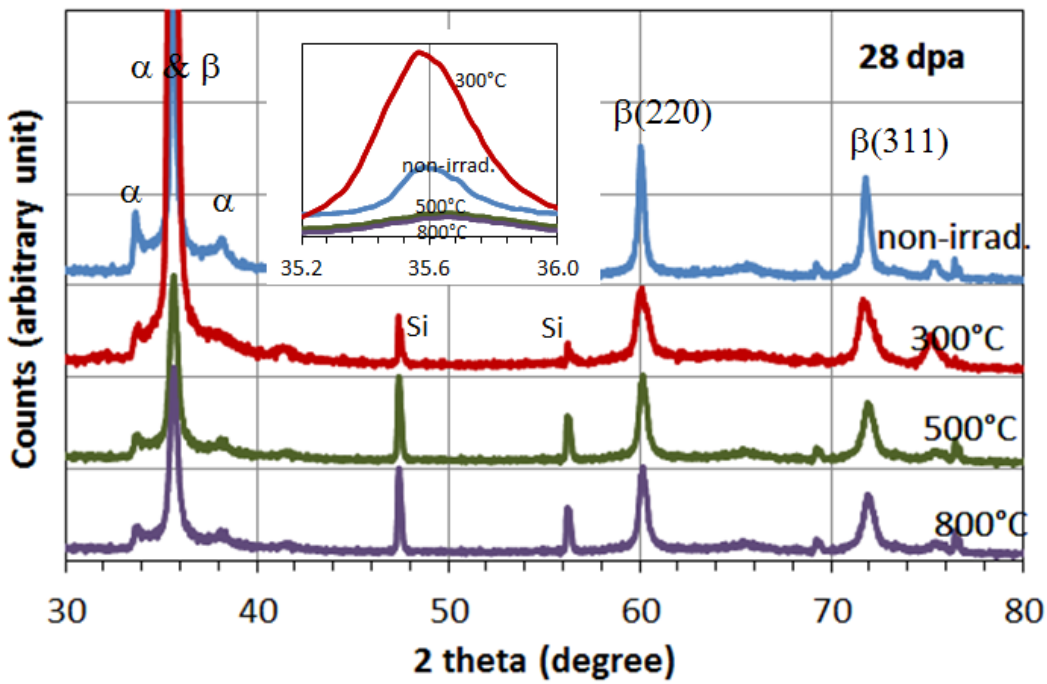

Fig. 4. XRD profiles of the ~28 dpa irradiated composites.

The results in Table 1 are graphically summarized in Fig. 6. The macroscopic length change is independent of irradiation fluence between ~28 and ~70 dpa and appears to be in a saturation regime. The magnitude of length swelling is inversely proportional to the irradiation temperature, which has been well known for CVD SiC and nuclear grade SiC/SiC composites in the point defect regime [1,3,8,9]. It is known that fairly good agreement between dimensional expansion and lattice constant expansion exists for SiC under neutron irradiation when irradiation conditions are at point defect regime (150 to 1000 °C) at intermediate neutron fluences (<5 dpa) [8,9] because very tiny interstitial clusters scattered in the matrix can account for both the XRD lattice swelling and volume swelling. However, there is a clear discrepancy between the macroscopic length change and the lattice space change of the HNLS composites in this study. This discrepancy has been previously reported in a couple of papers in the open literature that discussed about lattice space changes of high dose CVD SiC [8,10]. Considering the similar microstructure of the fiber and the matrix to that of CVD SiC, it is reasonable to believe that the same mechanism is account for the discrepancy in the high dose irradiated HNLS composites.

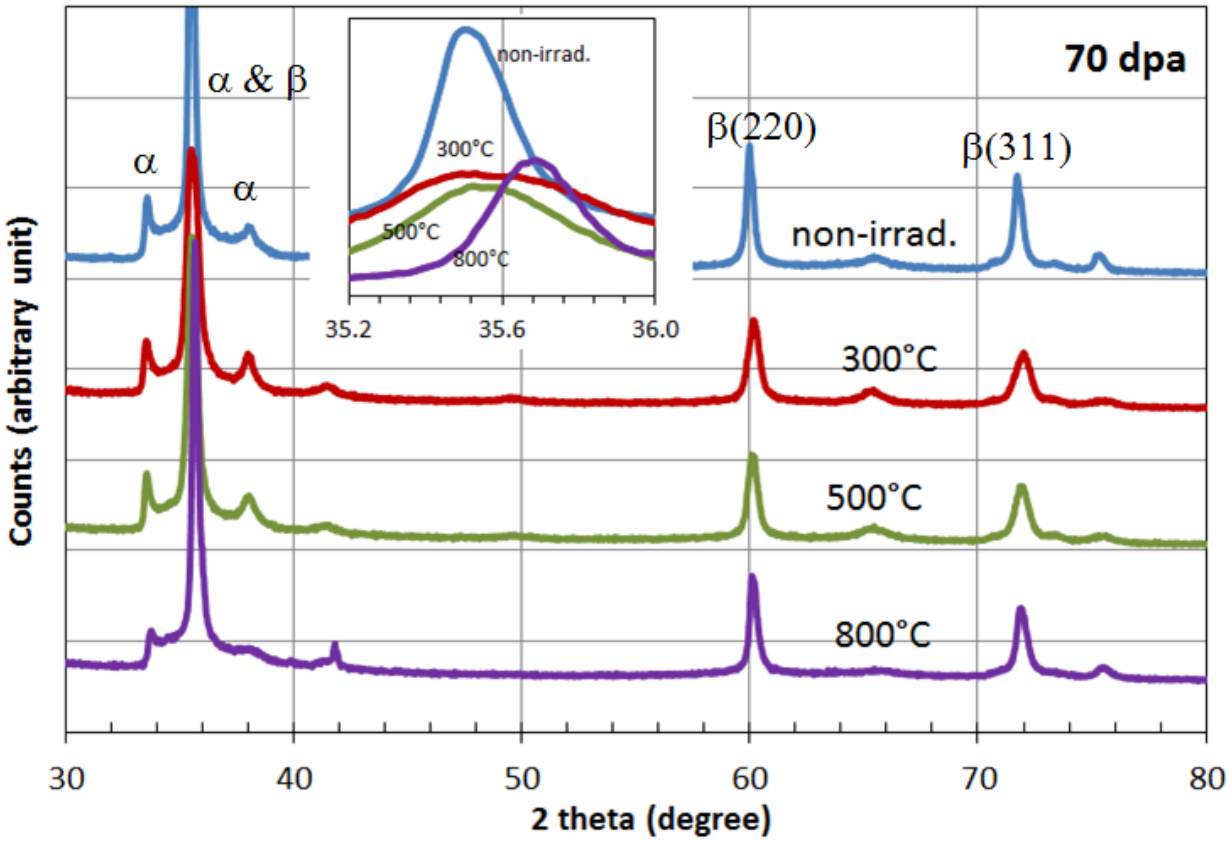

Fig. 5. XRD profiles of the ~70 dpa irradiated composites.

It should be noted that precise determination of lattice parameters requires a flat sample surface and a well-distributed internal standard (Si powder). In this study, the composite samples are not polished because of radiation contamination concerns. Moreover, the Si powder internal standard was sprinkled on top of the composites and was not well distributed. These factors all contribute to the errors associated with the lattice parameter determined by the XRD technique. It should also be noted that the two historical papers [8,10] that discussed about high dose CVD SiC are published in the 1970s. The materials in those studies, while claimed to be CVD SiC, might have more impurities than today's high purity CVD SiC or the CVI SiC matrix in the HNLS composites. Since impurities are known to affect the behavior of SiC materials under irradiation [9], readers should be skeptical about these historical results.

More recently, Yano and coworkers [11] reported lattice parameter changes and volume swelling of high dose neutron irradiated monolithic SiC. Their results showed similar trend of discrepancy between the two types of measurements. However, their material is not of high purity CVD SiC but has sintering aids, rendering direct comparison impractical.

Table 1. Summary of the d space change and the macroscopic length change following irradiation

	Irradiation condition		XRD		macroscopic	
Material	fluence (dpa)	Irrad. temp (°C)	d space (A)	% change	% liner change from dimension	standard deviation
HNLS composite w/ Si	Non-irradiated		4.360	-	-	-
HNLS composite w/o Si	Non-irradiated		4.366	-	-	-
HNLS composite	27.8	300	4.366	0.14	0.45	0.03
HNLS composite	28.2	500	4.356	-0.09	0.48	0.09
HNLS composite	28.0	800	4.359	-0.02	0.33	0.08
HNLS composite	40.7	800	4.363	0.06	0.23	N/A
HNLS composite	71	300	4.349	-0.25	0.64	0.09
HNLS composite	74	500	4.355	-0.11	0.48	0.03
HNLS composite	71	800	4.352	-0.18	0.33	0.04
HNLS bare fiber	Non-irradiated		4.360	-	-	-
CVD SiC	Non-irradiated		4.357	-	-	-
CVD SiC, 1975[10]	50	550	4.356	-0.09	0.43	N/A
CVD SiC, 1977 [8]	12	1000	-	0.03	0.14	0.05

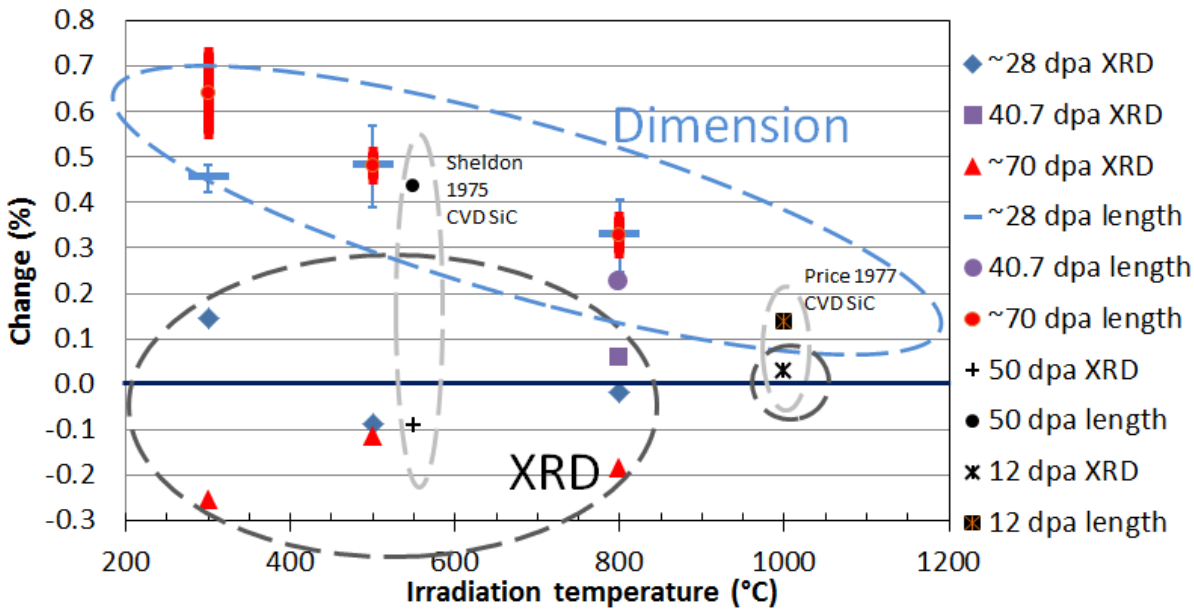

Fig. 6. Lattice parameter changes and macroscopic length changes of SiC materials at various irradiation conditions.

CONCLUSIONS

In summary, our XRD results of high dose neutron irradiated HNLS SiC/SiC composites show very little swelling or even shrinkage of lattice d space while macroscopic length swelling for the same samples is observed. Similar behaviors have been reported for high dose neutron irradiated CVD SiC [8,10] and hot pressed SiC [11]. However, the impurities of the materials used in the literature papers and the uncertainties in lattice space determined in this study, caused by the high sample surface roughness, make it difficult to draw a sound conclusion. More work is needed to verify whether the observed discrepancy is true and the cause of it.

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