MECHANICAL PROPERTIES OF ADVANCED SIC FIBER COMPOSITES IRRADIATED AT VERY HIGH TEMPERATURES – Y. Katoh, K. Ozawa, L.L. Snead (Oak Ridge National Laboratory), T. Hinoki (Kyoto University), Y.B. Choi (Hiroshima University), A. Hasegawa (Tohoku University)

OBJECTIVE

This work addresses several important aspects of the effect of neutron irradiation on mechanical properties of advanced SiC/SiC composites produced through chemical vapor infiltration (CVI). First, the effect of irradiation at temperatures exceeding 1000ºC is determined. Second, the influences of different SiC fibers and interphase thicknesses on post-irradiation mechanical properties are addressed. Finally, the effect of neutron irradiation on the matrix cracking stress is addressed.

SUMMARY

Six different composite materials with various near-stoichiometric silicon carbide (SiC) fiber reinforcements and pyrolytic carbon or SiC/pyrolytic carbon multilayer interphases were neutron-irradiated to ~$6x10^{25}$ n/m2 (E > 0.1 MeV) at nominal temperatures of 800ºC and 1300ºC, and tested for tensile properties at room temperature. Only insignificant or very minor modifications to the tensile strength were admitted in all materials. However, two-parameter Weibull statistical analysis on relatively large specimen populations revealed minor but significant strength degradation for some composites. 50 – 150 nm appeared to be within the optimum PyC interphase thickness range for both fiber types in terms of tensile properties. The misfit stresses present in the unirradiated samples were significantly reduced after irradiation. The change in misfit stress was attributed to the irradiation-induced modification of coefficient of thermal expansion. True matrix cracking stress estimated from the proportional limit stress and misfit stress did not appear to degrade by neutron irradiation.

PROGRESS AND STATUS

Introduction

Silicon carbide (SiC) continuous fiber-reinforced SiC matrix (SiC/SiC) composites are promising, commercially available materials for fusion applications. The advantage of SiC/SiC composites as fusion reactor materials comes mainly from the exceptional radiation stability, high temperature performance, and low activation properties inherent to SiC.[1, 2] Moreover, recent research and development of SiC/SiC composites for advanced fission energy systems accelerate the design and application technology development toward the deployment of these materials for nuclear services.[3] An extensive neutron irradiation campaign designated RB-18J was carried out in US/Japan fusion blanket/materials collaboration program for the purposes of 1) gaining fundamental understanding of irradiation effects in SiC composites and their constituents in aggressive, fusion-relevant conditions, 2) determining the effects of neutron irradiation on various properties of new generation materials, 3) advancing constitutive modeling of irradiation effects in composites, and 4) determining irradiated engineering properties in support of blanket systems research and development. In this experiment, a variety of composite materials fabricated with different near-stoichiometric SiC fibers, fiber/matrix interphases, and matrix materials were evaluated for mechanical and physical properties following neutron irradiation up to ~7 dpa at temperatures nominally in an 800-1300ºC range.

This paper addresses several important aspects of the effect of neutron irradiation on mechanical properties of advanced SiC/SiC composites produced through chemical vapor infiltration (CV). First, the effect of irradiation at temperatures exceeding 1000ºC is determined. The previous reports indicates relatively minor but potential degradation of mechanical properties, in particular the matrix cracking stress, after low dose irradiation at very high temperatures for materials which had been proven to be radiation-stable up to ~10 dpa at below ~800ºC.[4] Second, the influences of different SiC fibers and interphase thicknesses on post-irradiation mechanical properties are addressed. Majority of the published data on irradiation effect on advanced SiC/SiC composites are those for Hi-Nicalon™ Type-S

(HNLS) fiber composites.[5-8] Irradiation performance of the composites with different type commercial SiC fiber is comparatively determined. The optimum pyrocarbon interphase thickness range for use in high radiation environment of composites in these classes is discussed. Moreover, the effect of neutron irradiation on the matrix cracking stress is addressed. The potential irradiation-induced degradation of proportional limit stress (PLS), roughly corresponding to the matrix cracking stress, of advanced SiC/SiC composites has been pointed out; however, previously reported effect of irradiation on PLS has been inconsistent. In this paper, this issue is clarified based on the misfit stress analysis.

Experimental

Materials irradiated and examined are CVI SiC matrix composites reinforced with two-dimensional (2D) woven fabrics of either Hi-Nicalon™ Type-S (Nippon Carbon Co., Tokyo, Japan) or Tyranno™-SA3 (Ube Industries, Ltd., Ube, Japan), as summarized in Table 1. Fiber coatings with pyrocarbon (PyC) or PyC/SiC multilayer were applied to form the adequately weak interphase between the fibers and matrices. The PyC coating thickness was nominally 50 nm or 150 nm. In the multilayer interphase, details of which are found elsewhere,[8] incorporates a nominally 20 nm-thick PyC innermost layer which serves as the sliding interphase. The interphase coating and matrix densification were provided by Hypertherm High-Temperature Composites, Inc. (Huntington Beach, CA)

Table 1: Summary of composite materials studied.

Designator	Reinforcement	Interphase	Matrix
SA3/ PyC150	Tyranno-SA3 7.5 micron (SA3-S1I16PX), 2D Plain Weave (PSA-S17I16PX), 17x17 tpi, 0º/90º	PyC(150nm)	CVI-SiC
SA3/ PyC50	Tyranno™-SA Grade-3 7.5 micron (SA3-S1I16PX), 2D Plain Weave (PSA-S17I16PX), 17x17 tpi, 0º/90º	PyC(50nm)	CVI-SiC
SA3T/ PyC150	Tyranno™-SA Grade-3 10 micron (SA3-S1F08PX), 2D Plain Weave (PSA-S17F08PX), 17x17 tpi, 0º/90º	PyC(150nm)	CVI-SiC
HNLS/ PyC150	Hi-Nicalon™ Type-S 900 denier (#383213), 2D Plain Weave (HNS9P2424), 24x24 tpi, 0º/90º	PyC(150nm)	CVI-SiC
HNLS/ PyC50	Hi-Nicalon™ Type-S 900 denier (#383213), 2D Plain Weave (HNS9P2424), 24x24 tpi, 0º/90º	PyC(50nm)	CVI-SiC
HNLS/ ML	Hi-Nicalon™ Type-S 1800 denier, 2D-Satin Weave, 16x16 tpi, 0º/90º	5x[PyC(20nm)/ SiC(100nm)]	CVI-SiC

It is worth noting that non-standard fabrics or fibers were used for some of the composites studied. For the PyC interphase HNLS composites, 24x24 thread-per-inch (TPI) fabrics with 250 filament yarns were used instead of the standard 16x16 TPI fabric with 500 filament yarns. The use of finer weave fabrics increased the interlaminar porosity resulting in substantially reduced interlaminar strength.[9] For the SA3 composites, fabrics of 800 filament yarns of thick fibers (nominally 10 micron diameter) were used in addition to the fabrics of the standard 1600 filament yarns of 7.5 micron diameter fibers.

Irradiation was performed in the RB* facility located in the reflector beryllium position of High Flux Isotope Reactor (HFIR), Oak Ridge National Laboratory (ORNL). The nominal irradiation temperatures are 800ºC and 1300ºC. There is evidence that some of the samples in the 800ºC zone had received irradiation at significantly lower temperatures; however, most of the composite samples are believed to have been irradiated at the vicinity of 800ºC based on the thermocouple reading . The 1300ºC zone lost thermocouples at the early irradiation and was operated to maintain the highest design temperature after then; therefore, the actual irradiation temperature may likely be higher than 1300ºC. The average fast (E

> 0.1 MeV) neutron fluence for the 800ºC and 1300ºC zones are estimated to be ~5.9 and ~5.8 x 1025 n/m2 , respectively.

Tensile properties were examined at room temperature using straight beam specimens which measure 40 mm x 4 mm x 2 mm per general standard test practice in ASTM C1275-00. Strain was determined by averaging the readings from a pair of strain gauges attached to both faces within the gauge section. The intermittent unloading/reloading sequences were incorporated for extracting information related with the residual thermal stress and interfacial sliding stress. All the tensile specimens were measured for elastic modulus by impulse excitation and vibration method according to ASTM C1259-01. Fracture surfaces were examined by scanning electron microscopy following the tensile test.

Results

The tensile stress-strain properties before and after irradiation are shown in Fig. 1. All six materials exhibited pseudo-ductile tensile fracture behavior before irradiation, and such behavior was not altered after irradiation at either 800ºC or 1300ºC. The Hi-Nicalon HNLS composites exhibited an extensive non-linear strain with an exception of the multilayer interphase composite. The strain to failure exceeding 0.5% is exceptionally large for these composites and may be attributed to the poor matrix densification. The multilayer interphase can be considered a PyC interphase of ~20 nm thickness as far as fast fracture properties are concerned. Therefore, the relatively low strength and the premature failure observed for the multilayer interphase composite may be attributed to the excess interfacial friction due to insufficient interphase thickness to accommodate adequate interfacial sliding.[6, 10] It is noted that the non-linear strain is slightly enlarged in the irradiated HNLS, multilayer interphase composite. The SA3 composites exhibited similar tensile behavior regardless of interphase thickness (50 or 150 nm), fiber diameter, and irradiation condition. The strain to failure for these composites appeared to be in a 0.2 – 0.3% range, typical to SA3 fiber, CVI SiC matrix composites.

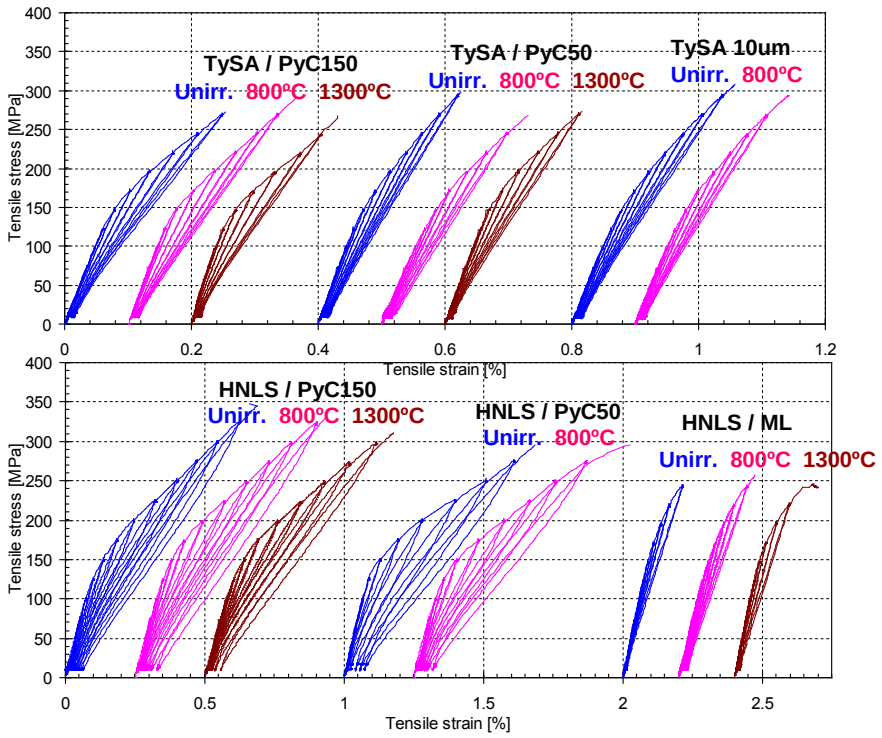

Fig. 1: Representative stress-strain curves recorded during tensile tests of six different SiC/SiC composites in unirradiated and irradiated conditions.

The results of sonic modulus and tensile properties determination are graphically summarized in Fig. 2. The decrease in elastic modulus, which is expected to occur to a very slight extent at these irradiation temperatures, either by vibration or tensile test appeared to be within the range of data scatter. Either PLS or ultimate tensile stress (UTS) did not undergo obvious change. However, the UTS of the HNLS and the 10 micron diameter SA3 composites may have degraded slightly.

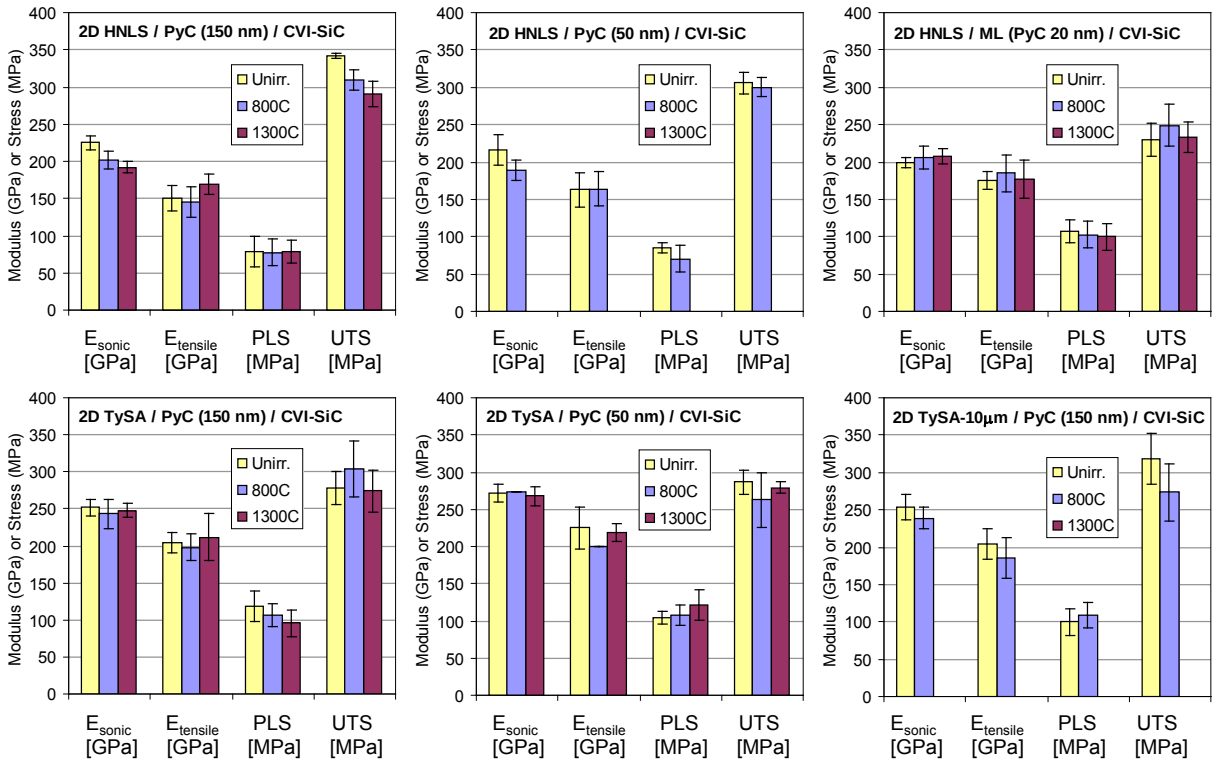

Fig. 2: Summary of the tensile properties and sonic modulus values in unirradiated and irradiated conditions. E_{sonic} and $E_{tensile}$ denote Young's moduli determined by sonic resonance and tensile tangential fit, respectively. Error bars represent one standard deviations.

Fracture surfaces of the 150 nm PyC interphase composites with HNLS and SA3 fibers are compared in Fig. 3 before and after irradiation. The fractographs reveal relatively long fiber pull-outs for the HNLS composites and much shorter fiber pull-outs for the SA3 composites, both of which do not noticeably change after irradiation at either temperature. Moreover, fracture surfaces of the individual fibers, typically consisting of rather indistinctive fracture mirror and a river pattern, did not show any sign of fiber strength change due to irradiation.

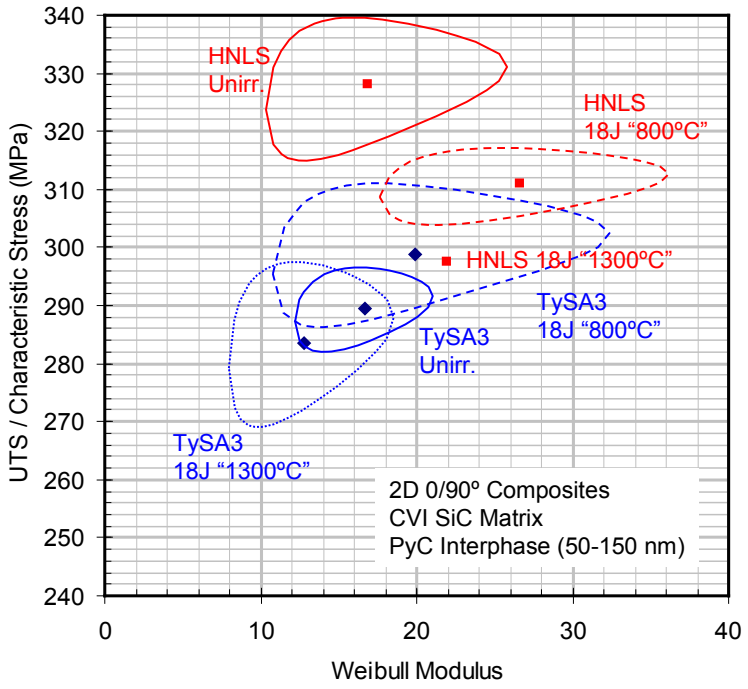

Fig. 3: Fracture surfaces of the 150 nm-thick PyC interphase composites with Hi-Nicalon™ Type-S and Tyranno™-SA3 reinforcements.

Discussion

The present result appeared to be consistent with the general perception that the stoichiometric SiC fiber, CVI SiC matrix composites do not significantly degrade their mechanical properties by irradiation to the intermediate fluence levels (e.g., ~10 dpa) at temperatures below ~800ºC. It also suggested that such trend retains true to irradiation temperature largely exceeding 1000ºC. However, in the previous studies, potential strength modification could not be much discussed because of the very limited statistics in contrast to the inherent scatter of strength of ceramic composites. Here, two-parameter Weibull statistics are examined for the UTS of both HNLS and SA3 composites. Because the tensile properties appeared very similar for the nominally 150 nm and 50 nm PyC interphases, UTS data for both interphases were combined for greater number of data. The plot, shown in Fig. 4 as the 95% confidence parameter bound rings, indicates fairly high Weibull shape parameters of 16 – 17 for the unirradiated condition. Both Weibull parameters were about the same for the two different PyC interphases in either fiber composite, indicating that the combining the different interphase thicknesses did not disturb the statistics. The result indicates that the UTS change of HNLS composites after irradiation at 800ºC may be statistically significant, although the decrease in average characteristic UTS value is only ~5%. On the other hand, the changes in UTS of SA3 composites appear insignificant at both irradiation temperatures. Because the UTS is determined primarily by fiber strength, the result implies that the SA3 fiber is more radiation resistant.

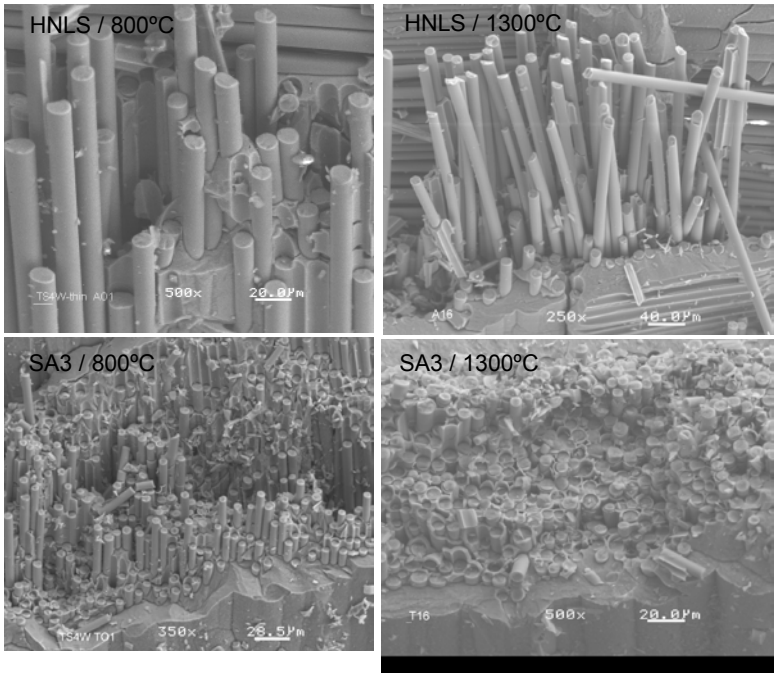

Fig. 4: Weibull statistic parameters for the UTS of 50-150 nm-thick PyC interphase composites in unirradiated and irradiated conditions. The parameters were determined by the maximum likelihood analysis. The rings indicate 95% confidence bounds.

Among six different materials examined in this work, only the HNLS composite with multilayer interphase exhibited the significant premature failure behavior, or the composite fracture far before the matrix crack saturation is achieved. Such erratic behavior has been reported for SiC/SiC composites with very thin interphases, in a more pronounced way in a uni-direction architecture, and is believed to be caused by the excess frictional stress for interfacial sliding.[6, 10] A closer examination of the stress-strain behavior of the HNLS multilayer composite, Fig. 1, reveals the greater extent of non-linear elongation after irradiation. Similar trend has been reported in previous work for a uni-directional composite with nominally the same fiber and interphase.[6] Thus, although the macroscopic modification of tensile properties by neutron irradiation did not appear substantial, there is rather a clear indication that the interfacial sliding property has been altered. Carbon materials are known to degrade mechanical properties by accumulation of displacement damage in excess of certain so-called “turn around” fluence levels and the degradation gets noticeably accelerated at higher irradiation temperatures. Therefore, in order to have the optimum interfacial properties retained during high fluence irradiation, the preferred interphase thickness may be smaller for composites for radiation services than for other applications so that stronger post-irradiation interfacial sliding stress may be achieved.

The PLS approximately correspond to the matrix cracking stress, or the composite stress at which at least one transverse matrix crack is developed and starts to open. Therefore, the PLS will likely give design stress guidelines for applications involving prolonged service durations. Interestingly, there have been conflicting reports with regard to the effect of neutron irradiation on the PLS; slight but significant reduction in the PLS has been reported in some works whereas no significant change has been reported in others.[4-6, 11, 12]

The matrix cracking stress is generally influenced by the residual thermal stress in a significant manner.[13] The near-stoichiometric SiC fibers reportedly possess the coefficient of linear thermal expansion (CTE) slightly greater than that of vapor-deposited high purity SiC. For example, the manufacturer-claimed CTE of HNLS fiber is 5.1×10^{-6} K^{-1} (RT-500ºC) as compared to 3.8×10^{-6} K^{-1} for CVD SiC in the same temperature range, giving substantial axial compressive and tensile residual stresses to matrices and fibers, respectively, upon cooling from the matrix infiltration temperature. The CTE misfit stresses, estimated from the regression analysis of the tensile reloading segments, appeared to be ~40 MPa for all the SA3 and multilayer interphase HNLS composites and ~60 MPa for PyC interphase HNLS composites in an unirradiated condition. The greater misfit stresses in the PyC interphase HNLS composites are considered to be reflecting the lesser extent of matrix infiltration. In the irradiated materials, these misfit stresses appeared to have significantly reduced, as shown if Fig. 5. Potential reasons for the reduced misfit stress include irradiation creep and modification of CTE of the constituents. With the irradiation temperature of ~1300ºC, which is close to or even higher than the matrix processing temperature, irradiation creep does not explain the misfit stress reduction. It is not clear whether the mechanism of CTE modification is structural modification of the impure fibers or radiation defect accumulation in SiC crystals.

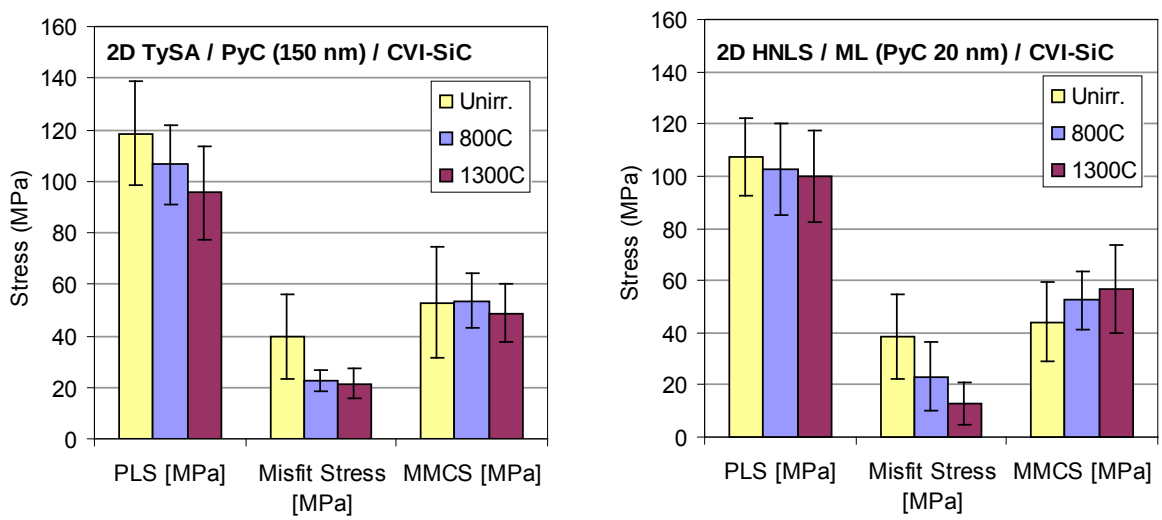

Fig. 5: Misfit stress and true “mini-matrix” cracking stress (MMCS, see text for explanation) estimated for selected composites based on the tensile reloading regression analysis.

Under an in-plane tensile loading to 0/90º 2D composites, cracks are believed to initiate typically within the matrix encapsulating the 90º fiber tows (90º “mini-matrix”). Tensile stress in such elements, σ_{mmx}, can be described by:

$$\sigma_{mmx} = \frac{\sigma_c + \sigma_{th}}{E_c}\left(\frac{E_c - f_{mc}E_{mc}}{1 - f_{mc}}\right) \qquad (1)$$

where σ_c = composite stress, σ_{th} = residual stress, E_c = composite modulus, f_{mc} and E_{mc} = volume fraction and modulus of 0º mini-composite elements, respectively.[14] The result of misfit stress and mini-matrix cracking stress analyses, provided in Fig. 5, indeed indicates that the detrimental effect of neutron irradiation on the true matrix cracking stress is inadmissible. Similar analysis on the PyC interphase HNLS composites provided only invalid result due to the poor matrix infiltration.

Conclusions

The effect of neutron irradiation on in-plane tensile properties of near-stoichiometric SiC fiber, CVI SiC matrix composites was determined. The following outstanding results were obtained.

1) Only insignificant and/or very minor modification to the tensile strength were admitted following irradiation to ~6 dpa nominally at 800ºC and 1300ºC.

2) Two-parameter Weibull statistics analysis revealed no significant irradiation effect on strength of the SA3 fiber composites, and significant yet minor strength degradation for the HNLS fiber composites.

3) 50 – 150 nm appeared to be within the optimum PyC interphase thickness range for both fiber types in terms of tensile properties. However, the optimum interphase thickness range may be altered with high fluence irradiation at high temperatures.

4) CTE misfit stresses present in the unirradiated samples were significantly reduced after irradiation. Irradiation-induced CTE modification is the likely reason.

5) True matrix cracking stress estimated from the PLS and misfit stress did not appear to degrade by neutron irradiation.

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