ANALYSIS OF NEUTRON IRRADIATION EFFECTS ON THERMAL CONDUCTIVITY OF SIC-BASED COMPOSITES AND MONOLITHIC CERAMICS - G. E. Youngblood and D. J. Senor (Pacific Northwest National Laboratory)*

OBJECTIVE

The objective of this work is to examine SiC composites fabricated by various processing methods designed to improve composite thermal conductivity. It is desired to increase the thermal conductivity of these composites to meet requirements for advanced fusion energy systems. Specifically, this paper will analyze data reported by Senor, et al., in Fusion Technology [1] and orally presented at the 1996 American Nuclear Society Annual Meeting, 16-20 June, Reno NV and at the Fifth Symposium on Fabrication and Properties of Ceramics for Fusion Energy and Other High Radiation Environments, American Ceramic Society 99th Annual Meeting, 5-7 May, 1997, Cincinnati OH.

SUMMARY

After irradiation of a variety of SiC-based materials to 33 or 43 dpa-SiC at 1000°C, their thermal conductivity values were degraded and became relatively temperature independent, which indicates that the thermal resistivity was dominated by point defect scattering. The magnitude of irradiation-induced conductivity degradation was greater at lower temperatures and typically was larger for materials with higher unirradiated conductivity. From these data, a K_{irr}/K_{unirr} ratio map which predicts the expected equilibrium thermal conductivity for most SiC-based materials as a function of irradiation temperature was derived. Due to a short-term EOC irradiation at 575° ± 60°C, a duplex irradiation defect structure was established. Based on an analysis of the conductivity and swelling recovery after post-irradiation anneals for these materials with the duplex defect structure, several consequences for irradiating SiC at temperatures of 1000°C or above are given. In particular, the thermal conductivity degradation in the fusion relevant 800°-1000°C temperature range may be more severe than inferred from SiC swelling behavior.

REVIEW

The performance of a variety of SiC-based composites and monolithic ceramics in the unirradiated, thermal annealed and irradiated conditions was characterized by determining their thermal conductivity values. The irradiation was conducted in the EBR-II reactor to doses of 33 and 43 dpa-SiC (185 EFPD) in an uninstrumented capsule designed to operate at 1000°C. Thermal annealed control specimens were held at 1010°C for 165 days to approximately duplicate the thermal exposure of the irradiated specimens. Through-the-thickness thermal diffusivity was measured generally over the temperature range 400° to 1150°C using the laser flash method, and converted to thermal conductivity using density data and calculated specific heat values. Table 1 presents a summary of the materials tested in this study.

The listed densities were determined by measuring the dimensions and weighing the

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unirradiated material. The baseline composite consisted of a Nicalon CG fiber reinforced matrix, nominally fully crystalline ß-SiC. Two alternate matrix materials, polymer impregnation with a 150 nm thick pyrolytic carbon (PyC) interface and a chemical vapor infiltrated (CVI) SiC and pyrolysis (PIP) and Blackglas SiC, were tested in combination with Nicalon CG fiber reinforcement. The resulting matrices were carbon- and oxygen-rich and at least partially amorphous. Two alternate fiber reinforcements (Tyranno and HPZ) and two alternate interfaces (15 nm PyC and 150 nm BN) also were tested in combination with the PIP SiC matrix. Two SiC-based particulate reinforced composites, SiC whisker (SiC_w) and SiC particulate (SiC_p) in combination with forced CVI and Blackglas matrices respectively, were tested. The monolithic ceramics included chemical vapor deposited (CVD) ß-SiC and two types of sintered α-SiC, Hexoloy SA and SX.

Table 1. SiC-based materials included in the test matrix.

Reinforcement	Fiber Architecture	Interface	Matrix	Measured Density (g/cm^3)	Vendor
Nicalon CG	0°/90°	150 nm PyC	CVI SiC	2.48 to 2.63	DuPont
Nicalon CG	0°/±86°	150 nm PyC	CVI SiC	2.68	DuPont
Nicalon CG	0°/90°	150 nm PyC	PIP SiC	2.20	Dow Corning
Nicalon CG	0°/90°	150 nm PyC	Blackglas	2.04	Allied Signal
Nicalon CG	0°/90°	15 nm PyC	PIP SiC	2.18	Dow Corning
Nicalon CG	0°/90°	150 nm BN	PIP SiC	2.21	Dow Corning
Tyranno	0°/90°	150 nm PyC	PIP SiC	2.10	Dow Corning
HPZ	0°/90°	150 nm PyC	PIP SiC	2.12	Dow Corning
SiC_w	-	-	CVI SiC	2.72	ORNL
SiC_p	-	-	Blackglas	2.73	Allied Signal
-	-	-	CVD ß-SiC	3.25	Morton
-	-	-	Hexoloy SA	3.16	Carborundum
-	-	-	Hexoloy SX	3.19	Carborundum

In general, the thermal conductivity values decreased with increasing temperature as expected for phonon conduction. Composites with higher bulk densities had higher thermal conductivity values. Composites with the more crystalline CVI matrix had thermal conductivity values roughly a factor of five greater than composites with the less crystalline and less pure PIP SiC matrix, and a factor of ten greater than composites with the amorphous Blackglas matrix. Fiber architecture and coating variations had no discernible influence on the thermal conductivity for these materials, and the long-term thermal annealing at 1010°C had little influence. The thermal conductivity values of the dense and high purity CVD ß-SiC exhibited the steepest temperature dependence and, depending upon temperature, were 8-15 times greater than the values for the CVI composites. The thermal conductivity values for the Hexoloy SA and SX sintered SiC were intermediate to that for the CVD ß-SiC and the CVI composites, with the SA material exhibiting conductivity values a consistent 10-20% higher than the SX material. The higher conductivity of the Hexoloy SA is attributed to the use of a boron sintering aid, whereas Hexoloy SX uses Y_2O_3.

Due to the irradiation doses, which were well above saturation doses, thermal conductivity values and their temperature dependences for all the monolithic materials and for the more crystalline CVI matrix composites were reduced significantly as expected. In contrast, the thermal conductivity values for the more amorphous PIP and Blackglas composites actually increased about 35% due to the irradiation at 1000°C which presumably caused partial crystallization and densification of the amorphous matrix. Details for each material listed in Table 1 are given in Reference 1.

In Figure 1, the thermal conductivity degradation for crystalline SiC and CVI SiC matrix composites, expressed as a ratio of the irradiated to the unirradiated thermal conductivity values (k_{irr}/k_{unirr}), is presented as a function of the irradiation/test temperature. To construct this map, data from Thorne, et al., Price, Rhode and Hollenberg, et al., were added to the data at 575° and 1000°C from this work.

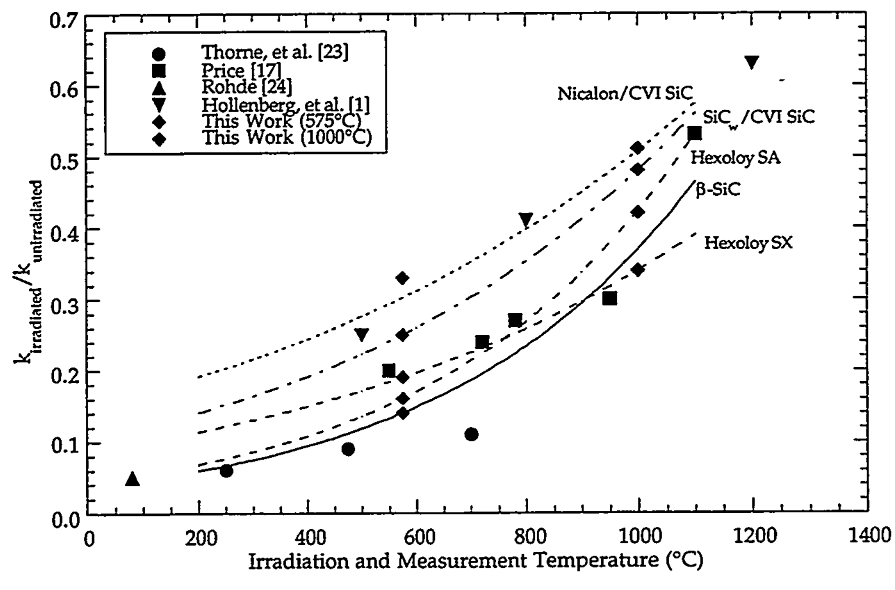

Figure 1. Thermal conductivity degradation as a function of irradiation/test temperature for crystalline SiC and CVI SiC matrix composites.

The general trend is for the k_{irr}/k_{unirr} ratio to increase as the irradiation/test temperature increases. For example, this ratio for ß-SiC ranges from 0.05 to 0.32 at 100°C and 1000°C, respectively. This trend reflects the relative dominance of the temperature independent irradiation point defect phonon scattering in the lower temperature range, while the temperature dependent intrinsic phonon-phonon scattering becomes relatively more important as the irradiation temperature increases. Significantly, the ratios can be separated into a family of roughly parallel best-fit curves which apparently depend upon purity, density and probably microstructural features. In this separation, the curve for CVD ß-SiC has the lowest ratio and represents the intrinsic irradiation behavior of SiC. In order of increasing ratios are curves for the sintered Hexoloy materials, the SiC_w particulate composite, and the continuous fiber reinforced CVI SiC matrix composite. From these curves, the thermal conductivity for irradiated crystalline SiC-based materials at any temperature can be predicted from measured values for unirradiated material. Most importantly, these curves establish fundamental limits to processing strategies, such as B-doping or thermal annealing treatments, which are designed to enhance the thermal conductivity of irradiated SiC-based materials. No thermal conductivity values greater than those predicted for irradiated CVD ß-SiC should be expected. As a general rule, the larger the thermal conductivity enhancement achieved through a processing strategy, the larger the relative degradation due to irradiation effects. The thermal conductivity degradation for irradiated SiC will always be dominated by the phonon scattering of radiation-induced point defects, primarily the vacancies.

The latter supposition is supported by the results from two different annealing studies given to the irradiated CVD ß-SiC material. In one study, a pair of passive CVD ß-SiC temperature monitor bars indicated that the capsule had been irradiated at a temperature much lower than the design temperature of 1000°C. In fact, the temperature monitor bars indicated via an isochronal annealing method that the irradiation temperature was 575° ± 60°C. In this method, bar lengths were measured after one-hour annealing times at successively higher temperatures. No length changes were observed to occur for annealing temperatures below 575°C; while the bar lengths decreased uniformly for the successively higher annealing temperatures once they exceeded the apparent 575°C irradiation temperature. After the final anneal at 1450°C (3 hours), the length recovery was only 50%. In similar annealing tests, others have observed at least 85% swelling recovery for irradiations at 800°C, so the limited 50% recovery was unexpected. This high level of residual swelling even after the 1450°C anneal is indicative of a substantial quantity of remaining stable irradiation defects, presumably due to the long-term 1000°C portion of the irradiation cycle. The approximately 50% swelling that actually recovered must have been primarily due to recovery of the short-term EOC 575°C irradiation defect structure. Thus, due to the operation of the reactor at reduced power for less than a day at the end of the normal 185 EFPD cycle, a duplex defect structure was induced in these CVD ß-SiC bars. One part of the duplex structure was characteristic of a long-term 1000°C irradiation; the other part was characteristic of a short-term 575°C irradiation, estimated to be representative of about a 0.1 dpa-SiC dose. This type of duplex defect structure also should have been present in all of the similarly irradiated SiC-based materials tested in this experiment.

In the second annealing study, the thermal conductivity degradation and recovery for one of the irradiated CVD ß-SiC diffusivity specimens was examined after a series of post-irradiation one hour anneals at 1150°, 1250°, 1350° and 1450°C. The effects on the thermal conductivity for this specimen are shown in Fig. 2.

The upper curve depicts the unirradiated thermal conductivity values as a function of temperature for high purity and dense ß-SiC; the lowest curve depicts the as-irradiated values. Note that the k_{irr}/k_{unirr} ratio at 575°C would be about 0.15 and would correspond to the data point shown for this material at that temperature in Fig. 1. The intermediate curves show the thermal conductivity temperature dependence for partially recovered ß-SiC since the thermal diffusivity was measured as a function of decreasing temperature after the one hour anneals. However, even after the 1450°C anneal about 50% of the thermal conductivity degradation remained. If the only defect structures generated during the irradiation were vacancies and small interstitial clusters, the 1450°C anneal should have been sufficient to restore the conductivity to near unirradiated values.

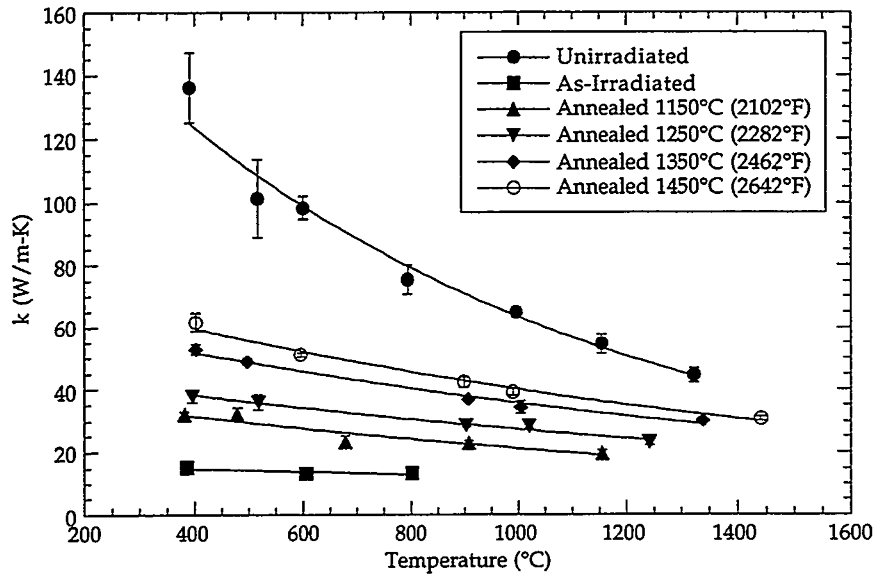

Figure 2. Effects of irradiation and multiple post-irradiation anneals on thermal conductivity of CVD ß-SiC.

The duplex irradiation defect structure proposed to explain 50% swelling recovery in the temperature monitor bars explains these thermal conductivity recovery data as well. The long-term 1000°C irradiation established a relatively stable network of interstitial dislocation loops, while the short-term 575°C irradiation established a defect structure characterized by smaller, less stable interstitial clusters. The vacancies for both types of interstitial configurations remain relatively isolated and distributed throughout the SiC lattice. The interstitial dislocation loops themselves are expected to be relatively coherent with the SiC crystal structure and are not expected to significantly degrade the thermal conductivity. The thermal conductivity and swelling recovery that occurred after anneals from 575°C up to about 1000°C was the result of interstitials not bound in the stable dislocation loops recombining with vacancies. With continued irradiation above about 1000°C, many interstitials would accumulate and stabilize into the dislocation loops which means that a corresponding number of the generated vacancies also would continue to accumulate. Eventually the vacancies become mobile at temperatures above about 1250°C. Nevertheless, the significant residual thermal conductivity degradation must be caused primarily by vacancies, either isolated or as small clusters scattered throughout the lattice, which provide the most effective phonon scattering sites.

The fact that only a small amount of recovery apparently occurred for that portion of the thermal conductivity degradation or of the swelling induced in SiC by the 1000°C irradiation has important consequences. Normally, the swelling versus irradiation temperature curve, which has decreasing values with increasing irradiation temperature and an extremely low minimum linear swelling of about 0.1% at 1000°C, is thought to saturate at a relatively low dose. Hence, after an initial small amount of swelling, ß-SiC has exhibited remarkable dimensional stability, especially during continued irradiation in the fusion relevant 800° to 1000°C temperature range. Above 1000°C the swelling should increase with further increase in irradiation temperature and should exhibit a dose dependent swelling maximum at about 1250°C, where vacancy mobility becomes important. However, the dose independence of the swelling minimum must be reconsidered in light of these recovery data. Based on the hypothesis that a stable interstitial defect structure can be formed in ß-SiC for a 1000°C irradiation, the dose dependent swelling maximum at 1250°C should shift to lower temperatures because of the continual buildup of the more stable interstitial dislocation loops. More importantly, the thermal conductivity degradation may not exhibit the same type of irradiation temperature dependence as the swelling with a dose independent minimum at 1000°C. Since in irradiated SiC the thermal conductivity degradation depends more upon the residual vacancy concentration than the interstitial defect configuration, the thermal conductivity degradation in the fusion relevant 800°-1000°C temperature range may be more severe than inferred from SiC swelling behavior.

FUTURE WORK

The irradiation and recovery effects for SiC-based materials irradiated in the COBRA 1A2 tests at 800°C will be analyzed.

REFERENCES

1. D.J. Senor, G.E. Youngblood, C.E. Moore, D.J. Trimble, G.A. Newsome and J.J. Woods, "Effects of Neutron Irradiation on Thermal Conductivity of SiC-Based Composites and Monolithic Ceramics," Fusion Technology 30(3), 943-955 (1996). Other pertinent references are given in this reference.