ELSEVIER

Journal of Nuclear Materials 307–311 (2002) 1200–1204

journal of nuclear materials

www.elsevier.com/locate/jnucmat

High thermal conductivity of graphite fiber silicon carbide composites for fusion reactor application

L.L. Snead [a,*], M. Balden [b], R.A. Causey [c], H. Atsumi [d]

[a] Oak Ridge National Laboratory, Oak Ridge, TN 37831-6138, USA
[b] Max-Planck-Institut für Plasmaphysik, Boltzmannstrasse 2, D-85748 Garching, Germany
[c] Sandia National Laboratory, MS 9402 Livermore, CA, USA
[d] Kinki University, Kowakae 3-4-1, Higashi-Osaka 577-8502, Japan

Abstract

The benefits of using CVI SiC/graphite fiber composites as low tritium retaining, high thermal conductivity composites for fusion applications are presented. Three-dimensional woven composites have been chemically vapor infiltrated with SiC and their thermophysical properties measured. One material used an intermediate grade graphite fiber in all directions (Amoco P55) while a second material used very high thermal conductive fiber (Amoco K-1100) in the high fiber density direction. The overall void was less than 20%. Strength as measured by four-point bending was comparable to those of SiC/SiC composite. The room temperature thermal conductivity in the high conductivity direction was impressive for both materials, with values >70 W/m K for the P-55 and >420 W/m K for the K-1100 variant. The thermal conductivity was measured as a function of temperature and exceeds the highest thermal conductivity of CVD SiC currently available at fusion relevant temperatures (>600 °C). Limited data on the irradiation-induced degradation in thermal conductivity is consistent with carbon fiber composite literature.

1. Introduction

It is commonly accepted that carbon fiber composites (CFC's) will have unacceptably high tritium retention and significant thermal conductivity reduction for application in fusion power reactors at intermediate temperatures ($T < 800$ °C). For higher temperature applications ($T > 800$ °C) the thermal conductivity degradation is mitigated, but the mechanical property degradation is accelerated, setting CFC useful lifetime into the 10–20 dpa range. Recently, the low thermal conductivity of silicon carbide fiber/silicon carbide matrix (SiC_f/SiC) composites, especially in the irradiated condition, raises questions regarding their viability as a first wall material. The purpose of this paper is to demonstrate, through a basic understanding of the phenomenon of tritium retention and thermal conductivity, that a composite material can be engineered with significantly reduced tritium retention with thermal conductivity and mechanical properties which satisfy the current fusion reactor concepts employing SiC composites.

1.1. Tritium retention

Tritium retention in graphite and silicon carbide are similar in many ways. Both materials have tritium diffusion coefficients that rise to measurable values only at very elevated temperatures [1–3], both materials have negative heats of solution for tritium [1,2], and both have tritium retention characteristics that depend on the crystallite size of the materials [2,4]. The diffusion coefficient for tritium in graphite as given by Causey [2] is: $D = 9.3 \times 10^{-5} \exp(-2.8\ \mathrm{eV}/kT)$ m^2/s. The diffusion coefficient for tritium in silicon carbide as given by Causey et al. [5] for beta silicon carbide is: $D = 9.8 \times 10^{-8} \exp(-1.89\ \mathrm{eV}/kT)$ m^2/s. Note the very high activation energy for the diffusion, suggesting migration

---

[*] Corresponding author. Tel.: +1-865 574 9942; fax: +1-865 241 3650.

E-mail address: sneadll@ornl.gov (L.L. Snead).

0022-3115/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-3115(02)01115-7

controlled by jumps from one trap site to another. Atsumi et al. [1] determined the solubility of hydrogen in graphite to be given by the expression $S = 6.4 \times 10^{-5} \exp(+0.2\ \mathrm{eV}/kT)$ atom fraction/atm$^{1/2}$. Causey et al. [5] reported the solubility of tritium in beta silicon carbide to be $1.7 \times 10^{-7} \exp(+0.61\ \mathrm{eV}/kT)$ atom fraction/atm$^{1/2}$. A negative heat of solution (solubility that decreases with increasing temperature) is an indicator of the chemical affinity of the hydrogen isotope to the host material. The inward permeation rate of tritium into these materials (product of diffusivity times/solubility) during exposure to hydrogen or tritium gas are among the lowest of all materials.

Atsumi et al. [4] have given direct proof of this in their study showing the apparent hydrogen solubility in graphite to vary inversely with the graphite perfection. Defects on the prism planes also provide a finite number of very deep traps (≈4.3 eV) that capture some of the tritium as it migrates along the crystallites. The number of deep traps also varies indirectly with the lattice parameter. Exposure to radiation damage decreases the graphite perfection (decreases the lattice parameter), increasing the apparent solubility and trap density [4,6,7].

It is possible that hydrogen also migrates along the crystal edges of silicon carbide. Evidence for this possibility comes from the study of Causey et al. [5] where beta silicon carbide samples with non-uniform crystal sizes were exposed to deuterium gas at elevated temperatures. Nuclear reaction profiling of the deuterium concentration showed enhanced retention on the sides of the samples with the smaller grains. Unlike graphite, radiation damage does not appear to affect the retention of hydrogen in beta silicon carbide [7]. At the present time, the reason for this is not understood. However, this immunity to radiation effects on trapping gives silicon carbide a significant advantage over graphite in minimizing tritium retention.

Fig. 1(a) demonstrates that the hydrogen solubility is reduced more than an order of magnitude as the degree of graphitization (crystalline perfection) is increased from 50% to 80% for $T_{\mathrm{irr}} \simeq 600$ °C. Moreover, Fig. 1(b) compares the tritium retention of an intermediate quality graphite and two high-quality CFC's. From these data it is seen that the tritium retention saturates at approximately 1000 appm for a standard nuclear graphite irradiated at <200 °C range, but apparently saturates at less than 100 appm for the higher perfection CFC's. The data of Fig. 1(a) and (b) are of particular interest because for typical C/C composites, the degree of graphitization of matrix material is significantly less than that of the highly oriented fibers, indicating that the majority of the tritium resides in the composite matrix. By replacing this (low perfection) graphite matrix with very low hydrogen solubility SiC, the high thermal conductivity of the fibers can still be utilized while the significant tritium retention problem associated with the matrix is avoided.

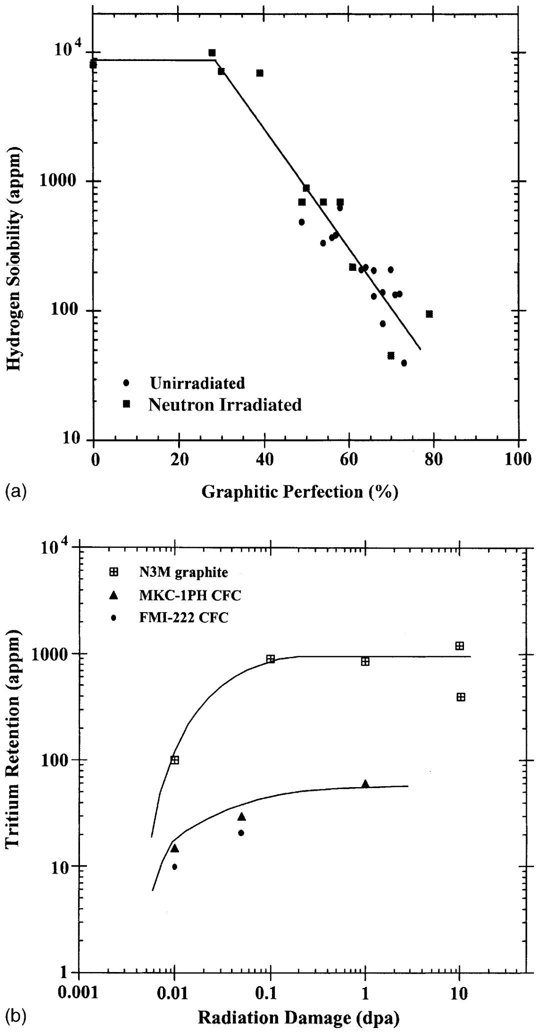

Fig. 1. (a) Effect of graphitic perfection on hydrogen solubility. Irradiation temperature was 200 and 600 °C [4]. (b) Effect on neutron dose on tritium retention of low and high quality graphite.

1.2. Thermal conductivity

Thermal conductivity degradation in graphite and C/C composites has been very well documented [8] and can decrease by over an order of magnitude at low fluence, depending on the irradiation temperature. This decrease in thermal conductivity typically saturates at a neutron fluence level between a few tenths and a few dpa, depending on irradiation temperature. Above room temperature, the process of phonon scattering significantly reduces the thermal conductivity in ceramics and graphite. At very high temperatures (≃1000 °C) this process is as effective at reducing thermal conductivity as defects associated with high-dose neutron irradiation.

A convenient way to compare the susceptibility of materials to irradiation-induced degradation in thermal conductivity is to compare their thermal defect resistances. This parameter is defined as follows:

$$1/K_{\mathrm{rd}} = 1/K_{\mathrm{irr}} - 1/K_{\mathrm{non-irr}}.$$

For both graphite [9] and most likely silicon carbide, the formation of vacancies and small vacancy clusters will dominate the phonon scattering, hence the thermal conductivity, in the temperature range from 200–1000 °C. Fig. 2 shows the thermal defect resistance parameter for pyrolitic graphite and silicon carbide as a function of irradiation temperature [10–12]. For both cases the neutron dose was sufficient to be above, or near, the point of saturation. Near room temperature the thermal defect resistance is about a factor of two less for the graphite, but as temperature is increases the defect resistance for the graphite rapidly decreases, while SiC slowly decreases with temperature. This is due to the limited interstitial mobility of SiC ($T_{\mathrm{crit}} \simeq 300$ K) [13,14] as compared to graphite ($T_{\mathrm{crit}} \simeq 20$ K) [15]. To reinforce this point, assuming the data of Fig. 2 and that thermal defect resistance was dominant, the thermal conductivity at 1000 °C would be $\simeq$100 W/m K for graphite and $\simeq$20 W/m K for silicon carbide. Clearly, the effect of irradiation on the thermal conductivity is more severe for SiC over the temperature range of interest to fusion.

1.3. Mechanical properties

Though development of this system has been limited, some authors [16–23] have reported these materials to have similar or higher strength as compared to SiC matrix/SiC fiber composites. Moreover, the flexural fracture toughness as measured by the area under the curve beyond macroscopic matrix micro-cracking is superior for the graphite fiber composites. A review on the subject of CVI SiC composites is given by Lara-Curzio [24].

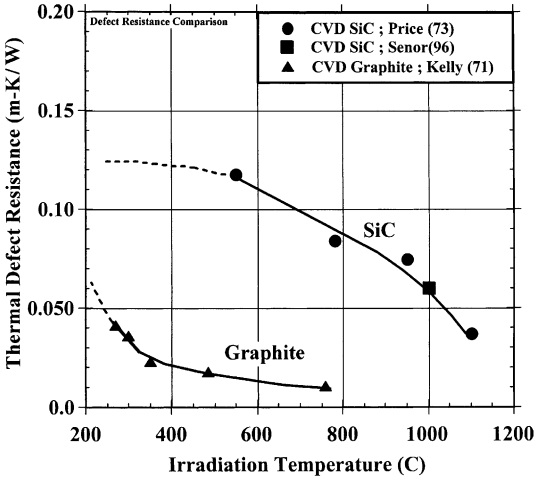

Fig. 2. Thermal defect resistance of pyrolitic graphite and silicon carbide for doses above saturation [10–12].

2. Experimental

Composite preforms were composed of a three-dimensional, unbalanced weave of Amoco K1100 and P55 graphite fibers. Both fibers are pitch derived from the same precursor, but have different graphitization temperatures, hence different degrees of crystalline alignment, perfection and thermal conductivity. The P55 fiber was woven in 2-*k* tows in the *x*- and *y*-directions while six 2-*k* tows of K1100 were stitched through the orthogonal weave in the *z*-direction (defined as the K1100 composite). A second perform with the same architecture used P-55 fibers in all directions (defined as the P55 composite). Preforms were rigidized with polymethylmethacrylate. The overall fiber volume fraction was 43.9% of which 7.1% was in the *x*- and *y*-directions and 85.7% was in the *z* direction. The graphite preform was machined into 4.45 cm diameter, 1.27 cm thick discs which were mounted in graphite holders for infiltration. The preform was then heated to 350 °C in an argon flow gas to burn out the PMMA binder. Preforms were then infiltrated with SiC using standard isothermal chemical vapor infiltration and forced-flow chemical vapor infiltration (FCVI) [25]. Room temperature bend testing was carried out on $0.3 \times 0.4 \times 5.0$ cm^3 bars with an upper and lower span of 1.9 and 3.8 cm, respectively. Thermal diffusivity was measured using a flash technique and conductivity calculated using the composite density and specific heat. A graphite standard was measured before each measurement ensuring the thermal diffusivity apparatus was operating to within a few percent error. The temperature dependent specific heat was calculated assuming the rule of mixtures. Irradiation was carried out in the high flux isotope reactor in peripheral tube rabbit capsules at a flux of $\simeq 8 \times 10^{18}$ n/m^2 ($E > 0.1$ MeV) and calculated sample temperatures between 400 and 800 °C. The samples were 6 mm in diameter and thickness. The axis of the samples was along the composite high conductivity direction. Atmosphere of the irradiation capsules was static helium.

3. Results and discussion

The potential for this composite in fusion applications is that it offers a high thermal conductivity composite with significantly lower tritium retention than the advanced carbon/carbon composites (C/C's) currently considered for plasma facing components. The thermal conductivity of the composite system can be engineered to be isotropic or optimized for high conductivity in a single direction, as needed. The three-dimensional CVD SiC/K1100 composite fabricated for this study yielded reasonably good strength and, from an analysis of the flexure curves [26] and fracture surfaces, possessed a fair amount of toughness. In the major fiber direction, the four-point bend strength was (267 ± 28) MPa which is comparable to CVI SiC/SiC fiber materials [24]. Strength of bend bars across the major fiber direction would be considerably reduced due to the reduced fraction of (P 55) fibers in this orientation.

The thermal conductivity of both SiC/graphite produced in this study is given in Fig. 3. Also shown is the thermal conductivity of a very high quality monolithic CVD SiC materials produced by Morton (now Rohm Haas), and the transverse thermal conductivity of an FCVI SiC/Type S Nicalon composite. As expected, due to the significantly higher thermal conductivity of the graphite fibers (≃950 and ≃120 W/m K at ambient for K1100 and P55, respectively) as compared to the SiC fiber (≃15 W/m K at ambient), the SiC/graphite composites have a much higher thermal conductivity in their major fiber direction. In their minor fiber direction, the thermal conductivity was ≃15 W/m K, or about the same as the SiC/SiC composite. At approximately 200 °C, the thermal conductivity of the K1100 composite exceeds that of the high quality CVD SiC while the P55 composite approaches this value at the highest temperatures measured. The filled points represent measured diffusivity data in Fig. 3.

The effect of low-dose irradiation at 400–800 °C on the P55/SiC composite is given in Fig. 4. Dimensional measurements yielded data consistent with irradiation-induced swelling of SiC. As expected, a large decrease in thermal conductivity has occurred for the three temperature/dose levels studied, with the largest decrease occurring for the higher dose, lower temperature specimens. As the dose is below that of saturation, and the data set is very limited, a quantitative comparison of the thermal conductivity degradation of the P55 composite with models and previous data from the graphite literature is not appropriate. However, from the data, the thermal defect resistance is comparable to, or perhaps larger, than expected from the literature on pyrolitic graphite. For the case of the 0.5 dpa irradiation, the thermal conductivity should be approaching saturation, indicating that the P55 material may possess more than twice the ≃15 W/m K minimum value of irradiated thermal conductivity called for in present day ARIES and TAURO design study. However, significant further study on the effect of irradiation is required. In particular, the thermal conductivity and the effects on non-isotropic swelling of the graphite fiber must be studied up to higher damage levels. As the thermal conductivity in these materials is carried primarily by the fibers, cracking of the fibers due to axial shrinkage and the effect of this on the thermal conductivity will need to be understood.

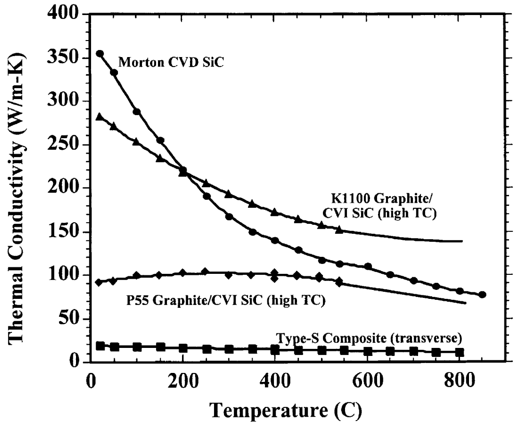

Fig. 3. Temperature dependent thermal conductivity of non-irradiated monolithic SiC, SiC/SiC and SiC/graphite composites.

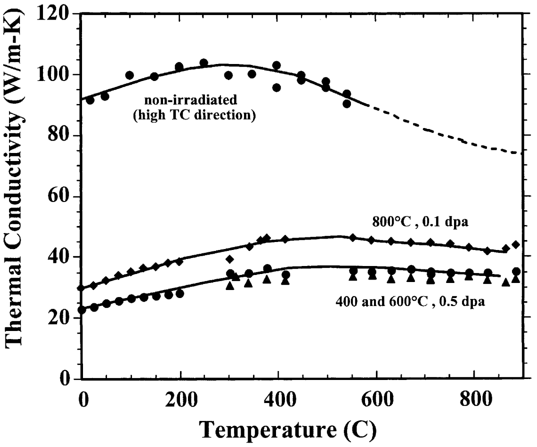

Fig. 4. Effect of low-dose irradiation at 400–800 °C on the thermal conductivity of SiC/graphite composite.

4. Conclusions

The potential of a silicon carbide matrix, graphite fiber composite for special purpose application in fusion systems has been presented. It is speculated, based on previous work on tritium retention in graphite and SiC, that this system will have significantly less tritium retention than present day high-quality CFC's. For the two materials of this study, the thermal conductivity at the fusion relevant operating temperature of 550 °C was ≃90 W/m K (P55 fiber composite) and 150 W/m K

(K1100 fiber composite.) This considerably exceeds the thermal conductivity of the present day CVI SiC/SiC composites at that temperature (≃12 W/m K). The effects of low-dose irradiation on thermal conductivity indicate a significant reduction in thermal conductivity, as expected from the graphite radiation effects literature. However, these preliminary data indicate the thermal conductivity still significantly exceeds the minimum value called for in design studies.

Acknowledgements

The authors would like to thank Marie Williams for assistance with thermal diffusivity measurements. Research sponsored by the Office of Fusion Energy Sciences, US Department of Energy under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

References

[1] H. Atsumi, S. Tokura, M. Miyake, J. Nucl. Mater. 155–157 (1988) 241.

[2] R.A. Causey, J. Nucl. Mater. 162–164 (1989) 151.

[3] V. Malka, H.D. Rohrig, R. Hecker, in: Proc. Conf. Tritium Technology in Fission, Fusion, and Isotope Applications, 1980, p. 102.

[4] H. Atsumi, M. Iseki, T. Shikama, J. Nucl. Mater. 212–215 (1994) 1478.

[5] R.A. Causey, W.R. Wampler, J.R. Retelle, J.L. Kaae, J. Nucl. Mater. 203 (1993) 196.

[6] R.A. Causey, Fus. Technol. 19 (1991) 1585.

[7] W.R. Wampler, R.A. Causey, Sandia Report SAND93-2007, October 1993.

[8] J.W.H. Simmons, Radiation Damage in Graphite, Vol. 102, Pergamon, 1965.

[9] R. Taylor, K.E. Gilchrist, L.J. Poston, J. Phys. Chem. Solids 30 (1969) 2251.

[10] B.T. Kelly, Carbon 9 (1971) 783.

[11] R.J. Price, J. Nucl. Mater. 48 (1973) 47.

[12] D.J. Senor, G.E. Youngblood, C.E. Moore, D.J. Trimble, G.A. Newsome, J.J. Woods, Fus. Technol. 30 (1996) 943.

[13] L.L. Snead, S.J. Zinkle, in: I.M. Robertson et al. (Eds.), Microstructure Evolution During Irradiation, MRS Symposium Proceedings, Vol. 439, Materials Research Society, Pittsburgh, 1997, p. 595.

[14] S.J. Zinkle, C. Kinoshita, J. Nucl. Mater. 251 (1997) 200.

[15] J.W. Corbett, Electron Radiation Damage in Semiconductors and Metals, Academic Press, New York, 1966.

[16] K. Nakano, J. Ceram. Soc. Jpn. 100 (4) (1992) 472.

[17] T. Noda, J. Nucl. Mater. 179–181 (1991) 379.

[18] E. Tani, K. Shobu, T. Watanabe, J. Ceram. Soc. Jpn. (1992) 596.

[19] H. Yoshida, J. Ceram. Soc. Jpn. 100 (4) (1992) 454.

[20] G. Camus, L. Guillaumat, S. Baste, Compos. Sci. Technol. 57 (1996) 407.

[21] M.R. Effinger, D.S. Tucker, T.R. Barnett, Ceram. Eng. Sci. Proc. 17 (1996) 316.

[22] M.C. Halbig, Ceram. Eng. Sci. Proc. 18 (1997) 547.

[23] A. Lacombe, J.M. Rouges, in: Space Programs and Technologies Conference '90', Huntsville, AL, 1990.

[24] E. Lara-Curzio, Comprehensive Composites Encyclopedia, Vol. 4.18, Elsevier, 2000, p. 533.

[25] T.M. Besmann, J.C. McLaughlin, H.T. Lin, J. Nucl. Mater. 219 (1995) 31.

[26] L.L. Snead, O.J. Schwarz, J. Nucl. Mater. 219 (1995) 3.