CONF-~~95~~951011-3

Effect of Sub-Minute High Temperature Heat Treatments on the Thermal Conductivity of Carbon-Bonded Carbon Fiber (CBCF) Insulation

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ABSTRACT

The thermal conductivity of carbon-bonded carbon fiber insulation in vacuum was determined before and after short duration heat treatments to model the effect of varying degrees of graphitization. Specimens of the insulation were heat-treated for 10, 15 and 20 seconds at 2673, 2873, 3073, and 3273 K. The dimensions and mass of each specimen was recorded before and after heat treatments. The thermal conductivity of the heat treated specimens was measured as a function of temperature up to 2273 K. These data are compared with previously measured specimens heat treated at the same temperatures for 1 minute and one sample heat-treated at 3273 K for 1 h. The thermal conductivity increases with both the heat treatment temperature and time at temperature. The thermal conductivity data has been modeled to obtain equations that predict the thermal conductivity of the insulation as a function of temperature ($673 \text{ K} \leq T \leq 3773 \text{ K}$) and heat treatment conditions of time ($0 \leq t \leq 20 \text{ s}$) and temperature (2673 K to 3773 K).

INTRODUCTION

Carbon-bonded carbon fiber insulation possesses a unique set of thermal and mechanical properties that permits use as a high-temperature insulating material in vacuum environments. Fabrication of the material has been described previously in detail [1]. During certain application conditions, the insulation may be exposed to thermal ramps (heating and cooling) with time spans ranging up to 20 seconds and peak temperatures in the range of 2200 K to about 4100 K. Mizushima [2] has shown that heat treatments as short as four minutes can result in partial graphitization. Thus, short duration high-temperature exposure may be expected to cause varying degrees of graphitization of the carbon fibers in the insulation. Such changes in the fiber microstructure would have a profound impact on the thermal conductivity of the insulation. The purpose of this study is to experimentally measure, explain and model the effect of shorter duration (up to 20 seconds) high-temperature exposures on the thermal conductivity of the insulation.

A total of 36 insulation specimens were heat treated in this study. Each specimen was heat treated once. There were twelve heat treatment runs, each beginning with three as-fabricated CBCF insulation specimens. Heat treatments lasted for either 10, 15 or 20 seconds at temperatures of 2673, 2873, 3073 or 3273 K. The thickness, diameter, mass, and room-temperature thermal diffusivity were measured for each test specimen before and after heat treatment. The thermal

diffusivity of two specimens from each heat treatment run was measured up to 2273 K after heat treatment. The third specimen was archived for future studies.

The thermal conductivity was calculated from the specific heat of carbon, bulk density of the test specimen, and thermal diffusivity data. The thermal conductivity data were then modeled to obtain equations that predict the thermal conductivity of the insulation as a function of temperature ($673 \text{ K} \leq T \leq 3773 \text{ K}$) and heat treatment conditions of time ($0 \leq t \leq 20 \text{ s}$) and temperature (2273 K to 3773 K). It is important to note that these models were developed from measurements in the temperature range 673 to 2273 K on insulation exposed for 10, 15 or 20 seconds at temperatures in the range 2673 to 3273 K. The accuracy of these equations is typically within $\pm 10\%$ of the experimental data under these conditions. Extrapolation of these equations to higher heat treatment and measurement temperatures could result in a higher, and yet undetermined, uncertainty. Accuracy for the as-fabricated material (typically $\pm 20\%$) is lower due to a very low thermal diffusivity. The model developed in this report is not suitable for exposure times greater than 20 seconds.

HEAT TREATMENTS

Heat treatments were carried out in a graphite tube furnace with flowing ultrahigh-purity argon gas (Oxygen: 0.5 ppm, Moisture: 0.0 ppm, Hydrocarbon: 0.0 ppm). Temperatures were determined by correlating furnace power levels with pyrometer readings. The pyrometer was carefully calibrated prior to the heat treatments in an arrangement designed to simulate the actual furnace setup. A diagram of the graphite furnace is shown in Fig. 1. In order to make short duration heat treatments, the furnace was modified to allow the addition of a push-rod. This push-rod was used to quickly slide a specimen capsule from the cool zone at one end of the furnace into the hot zone and then into the cool zone at the opposite end of the furnace. The exposure time was defined to be the time the specimen was in the hot zone. The time required for the specimen to heat up and cool down were initially assumed to be negligible due to the effectiveness of radiation heat transfer at these temperatures. The time required to reach the heat treatment temperature was later determined to be approximately 4.3 seconds, as discussed below.

Figure 1. Diagram of furnace used for heat treating the insulation. 1) graphite specimen capsule, 2) graphite push-rod, 3) carbon-felt push-rod bushing, 4) pyrometer, 5) graphite tube support, 6) window, 7) carbon furnace insulation, 8) hot zone of furnace 9) graphite heater element. (Drawing not to scale)

A diagram of the specimen capsule is shown in Fig. 2. The capsule was machined from graphite to hold seven specimens of the insulation (nominally 12.5-mm-diameter, by 1-mm-thick disks). The capsule is open at the leading end, and the specimens are held in place by an open-end cap at the other end. The three test

specimens are surrounded by four dummy specimens (two on the leading end and two on the cap end). The specimens were separated by thin graphite disks to uniformly distribute the furnace heat throughout the capsule. Following heat treatment, specimens were removed and characterized for thickness, diameter, mass, and density. Two specimens were inserted into a vacuum furnace for determination of thermal diffusivity as a function of temperature. The third test specimen has been reserved for x-ray diffraction analysis and microscopy studies.

DIMENSIONAL AND WEIGHT CHANGES

The thickness and diameter of each test specimen were measured before and after heat treatment using a digital caliper. The mass of each specimen was measured on an analytical balance before and after heat treatment. All measurement instruments have been calibrated within the past six months using standards from the National Institute of Standards and Technology. These data show a general trend, the fraction of weight loss increases with both heat treatment temperature and time. However, the total weight change is very small, typically less than 2%, and the scatter in this data is large.

THERMAL DIFFUSIVITY/CONDUCTIVITY

Thermal diffusivity measurements were made under high vacuum conditions (10^{-6} Torr) using the flash diffusivity system operated by the Carbon and Insulation Materials Technology Group in the Metals and Ceramics Division at Oak Ridge National Laboratory. Thermal conductivity values were calculated from the relationship $k = \alpha \rho C_p$, where k is the thermal conductivity, α is the thermal diffusivity, ρ is the bulk density, and C_p is the specific heat at constant pressure. Thermal diffusivity values were calculated using a parameter estimation technique developed by Koski [3]. The specific heat values used in these calculations are given in Table I.

The thermal conductivity of four specimens of the as-fabricated insulation is shown in Fig. 3. This plot demonstrates the typical specimen to specimen variability in the insulation and the typical experimental scatter observed in the thermal conductivity data. The thermal conductivity increases with increasing measurement temperature due to the contribution of radiation within the insulation.

Figure 2. Diagram of graphite specimen capsule used for heat treating specimens of the insulation. (Drawing not to scale)

TABLE I. The temperature dependence of specific heat of the insulation.

Temperature (K)	Specific Heat J/(kg · K)
298	733.0
373	930.3
473	1155
573	1338
673	1484
773	1601
873	1696
973	1772
1073	1865
1173	1886
1273	1929
1373	1965
1473	1995
1573	2021
1673	2043
1773	2062
1873	2078
1973	2093
2073	2105
2173	2116
2273	2125

The thermal conductivity increases as the furnace hot zone exposure time is increased. This is shown clearly in Fig. 4, where the thermal conductivity measured at 1073 K is plotted as a function of the time the specimen was exposed to 3273 K. The solid horizontal line represents the value of thermal conductivity after a 1 hour thermal exposure at 3273 K.

IMPROVED MODEL

The temperature dependence of thermal conductivity (λ_T) for fibrous insulation may be modeled using the relationship

$$\lambda_T = A f_s \lambda_S + \lambda_R + \lambda_G, \quad (1)$$

where A is the fraction of heat transfer in the parallel mode, f_s is the volume fraction of solid (approximately 0.1 for the insulation), λ_S is the thermal conductivity of the solid phase, λ_G is the thermal conductivity contribution due to the presence of a gas phase within the specimen (assumed here to be zero), and λ_R is the effective thermal conductivity due to radiation given by

$$\lambda_R = (16 n^2 \sigma / 3 \sigma_e) T^3, \quad (2)$$

Figure 3. The thermal conductivity increases with increasing measurement temperature due to the contribution of radiation within the insulation.

Figure 4. The thermal conductivity of the insulation measured at 1073 K is shown as a function of heat treatment time at 3273 K.

where n is the index of refraction ($n=1$), σ is the Stefan-Boltzmann constant [$5.6697 \times 10^{-8} \text{ W}/(\text{m}^2 \cdot \text{K}^4)$], σ_e is the extinction coefficient for the insulation, and T is the absolute temperature. The solid-phase thermal conductivity must be scaled to account for density and the fact that not all the solid phase contributes to the solid thermal conductivity. The temperature dependence of the thermal conductivity of graphite is typically modeled by

$$\lambda = A_1 \cdot T^{-\epsilon}, \quad (3)$$

where A_1 and ϵ are fitting parameters with $\epsilon=1$ for ideal graphite. For polycrystalline graphite with point defects, ϵ is between 0.5 and 1. Poor quality graphite with a significant population of extended defects has a value of ϵ of less than 0.5.

To model the sub-minute thermal conductivity data, it was decided to keep the radiation contribution consistent with previous results ($\sigma_e = 14000 \text{ m}^{-1}$) [4], and to modify the solid contribution with the relationship

$$\lambda_s = X A_1 T(\epsilon + Z) \quad (4)$$

where A_1 and ϵ are determined by modeling the thermal conductivity of as-fabricated specimens ($A_1 = 0.0232747$ and $\epsilon = 0.237966$), X and Z are (to be determined) functions of heat treatment time and/or heat treatment temperature. Thus, the functional form of the equation used to model the thermal conductivity of the insulation is given by

$$\lambda = X A_1 T(\epsilon + Z) + 2.1599 \times 10^{-11} T^3 \quad (5)$$

Equation 5 was fit to the thermal conductivity data for specimens heat treated at various temperatures for 10, 15 and 20 seconds. Figure 5 shows a plot of the resulting fitting parameter, Z , as a function of the heat treatment temperatures. Equation 6 gives the linear relationship between Z and the heat treatment temperature, T_m .

$$Z = 1.276492 - 0.0005659 * T_m \quad (6)$$

Equation 6 was substituted back into Eq 5 which was used to refit the data to find the relationship between X and the heat treatment conditions (Eqs 7 and 8). Figure 6 shows a plot of the fitting parameter X as a function of the heat treatment temperature for the 10, 15 and 20 second thermal conductivity data. The fitting parameter X was found to contain a time dependent term R . By definition, we know that $X=1$ when $t=0$, therefore, R must equal 1.26×10^{-5} when $t=0$. Initially, it was found that R equals this value for a time of 4.3 seconds. We were able to bring the R parameter data in line with the as-fabricated value by subtracting 4.3 seconds from the time in the furnace hot zone. This value of 4.3 seconds can be thought of as the time required by the specimen to reach the heat treatment temperature. Figure 7 shows the relationship between the parameter R , and the corrected time at temperature. Equations 7 and 8 give the relationship between X and the heat treatment temperature and time, t , of exposure.

$$X = R \exp(T_m * 0.004963) \quad (7)$$

$$R = 1.26115 \times 10^{-5} + 3.6166 \times 10^{-7} * t \quad (8)$$

Figures 8, 9 and 10 show the results of combining Eq 5, 6, 7 and 8 and refitting the thermal conductivity data for specimens heat treated for 5.7, 10.7, and 15.7 seconds, respectively. The prediction for as-fabricated thermal conductivity is included for comparison. Figure 3 shows the fit of this model to the as-fabricated data.

The quality of the fit of this model can be determined by plotting the residuals. Figures 11 and 12 show plots of the residuals as a function of temperature for heat treated specimens and as-fabricated specimens, respectively. Typical scatter in the residuals for the heat treated specimens lies between $\pm 10\%$. The standard deviation of the percent residuals for as-fabricated and heat treated specimens are shown in Tables II and III, respectively. The scatter in the residuals for as-fabricated specimens lies between $\pm 20\%$. This larger scatter is due to the allowable variations in the CBCF insulation, which results in a specimen-to-specimen variation in thermal conductivity.

CONCLUSIONS

The overall thermal conductivity of the insulation increases with heat treatment temperature and time at temperature. The functional form for the solid-phase thermal conductivity, used to model the temperature dependence of thermal conductivity of the insulation is $XA_1T^{(\epsilon+Z)}$. The constants A_1 and ϵ are determined from modeling the thermal conductivity of as-fabricated specimens, where $X = 1$ and $Z = 0$. The fitting parameter, X , is a function of both time and heat treatment temperature. The parameter X may be calculated using Eq. 7 and 8. The fitting parameter Z is a function only of the heat treatment temperature and may be calculated from the linear relationship Eq. 6. The predicted values are typically within $\pm 10\%$ of the measured values except for as-fabricated specimens where the agreement is within $\pm 20\%$. The larger uncertainty in the as-fabricated data is due to specimen-to-specimen variability in the material and the low thermal conductivity.

ACKNOWLEDGMENTS

Research sponsored by the Space and National Security Programs, Office of Nuclear Energy, Science and Technology, and the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, as part of the High Temperature Materials Laboratory User Program, Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp. for the U.S. Department of Energy under contract DE-AC05-96OR22464

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Figure 5. Fitting parameter Z as a function of heat treatment temperature.

Figure 6. The relationship between X and the heat treatment conditions (T_m and time) determined through a non-linear least squares fitting of Eqs. 7 and 8.

Figure 7. Fitting parameter R as a function of time at heat treatment temperature. A constant value of 4.3 seconds has been subtracted from the time in the hot zone of the furnace in order to bring the data in line with the as-fabricated value of R .

Figure 8. Fit of model to thermal conductivity data for specimens heat treated for 5.7 s (furnace hot zone exposure = 10 s).

Figure 9. Fit of model to thermal conductivity data for specimens heat treated for 10.7 s (furnace hot zone exposure = 15 s).

Figure 10. Fit of model to thermal conductivity data for specimens heat treated for 15.7 s (furnace hot zone exposure = 20 s).

Figure 11. Percent residuals for all heat treated data

Figure 12. Percent residuals for as-fabricated data

TABLE II. The standard deviation of the percent residuals from the fit of Eq. 5 to the thermal conductivity data for as-fabricated specimens.

Specimen ID	Standard Deviation (%)
B-54-4E	3.47
B-51-4E	3.68
B-49-1E	4.13
B-57-4F	11.0

TABLE III. The standard deviation of the percent residuals from the fit of Eq. 5 to the thermal conductivity data for heat treated specimens.

Heat Treatment Temperature (°C)	Heat Treatment Time(s)	Standard Deviation (%)
2673	5.7	4.86
2873	5.7	4.96
3073	5.7	5.99
3273	5.7	4.53
2673	10.7	6.55
2873	10.7	3.84
3073	10.7	2.03
3273	10.7	2.19
2673	15.7	5.45
2873	15.7	3.29
3073	15.7	4.33
3273	15.7	4.11

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