# UTILIZATION OF X-RAY DIFFRACTION DATA FOR PREDICTION OF CARBON-CARBON COMPOSITE THERMAL CONDUCTIVITIES

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## Introduction

Calculations of composite properties such as thermal conductivities can be made using classical micromechanical models, provided information on constituent properties, fiber architecture, fiber volume fraction, etc. is available. Frequently with carbon-carbon (C-C) composites, due to the high heat treatment temperatures used in the fabrication process and the tendency towards enhanced graphitization of the constituents with heat treatment, the conductivities of the individual constituents are not readily known. X-ray diffraction (XRD) data of several different carbon-carbon (C-C) composites and on reinforcement subjected to the same graphitization temperatures has been measured by the Aerospace Corporation and used by the author within submicromechanical mathematical models to predict the thermal conductivities of the C-C constituents. Composite characterization data, e.g. density, fiber architecture, fiber volume fraction, etc. measured by the Aerospace Corporation, Southern Research Institute (SRI), and the C-C fabricator, was used in micromechanical and multidirectional composite models to predict the C-C composite thermal conductivities. Thermal conductivities of the composites, measured by SRI, enabled a correlation between predicted and measured conductivities to be performed, thereby providing verification to the series of composite property models.

## Characterization Data

Two different types of C-C composites will be discussed here. The first type is fabric reinforced in which non-thermally stable fibers (Amoco's P-30X and Mitsubishi Kasei's K321) provided reinforcement for a high conductivity pitch matrix composite. The second type consists of Amoco's Self Reinforced Graphite (SRG) in a quasi-unidirectional orientation densified with high conductivity pitch-based matrix material. For both types of composites, graphitization temperatures well in excess of 2000°C were used. For the fabric reinforced composites, during the graphitization step witness fabric was placed in the furnace to allow it to experience the same temperatures for the same duration as the composites themselves. In this way, XRD data measured on the fabric alone is as representative of the structural characteristics of the fiber in the composites as is possible. Since the SRG experiences temperatures during its fabrication which are as high as that experienced by the SRG/carbon composites, the placement of witness SRG within the graph furnace was deemed unnecessary.

For the fabric reinforced composites, the Aerospace Corporation measured average crystallite domain lengths ($L_a$, $L_c$), and interlayer spacing ($d_{002}$) on both the composites and on the witness fabric. For the SRG/carbon composites, the average domain lengths and interlayer spacing were measured on the composites. Earlier measurements on undensified SRG by the Aerospace Corporation [1] were used to obtain structural characteristic of the SRG representative of that in the SRG/carbon composites. Table 1 provides a summary of the composite and reinforcement XRD data.

Table 1. Summary of Aerospace Corporation XRD data.

| Compos | Composite XRD | | | Fiber XRD | | |
|---|---|---|---|---|---|---|
| | $L_a$ nm | $L_c$ nm | $d_{002}$ nm | $L_a$ nm | $L_c$ nm | $d_{002}$ nm |
| K321/C | 58.5 | 38.0 | .3372 | 50.5 | 32.5 | .3376 |
| P30X/C | 52.0 | 38.0 | .3372 | 48.6 | 32.5 | .3375 |
| SRG/C | 90.5 | 61.8 | .3366 | 78.5 | 58.5 | .3366 |

Although the XRD data indicates that the K321 fibers and composites have longer crystallite domain lengths in the fiber axis direction ($L_a$), the d-spacing for the P-30X fibers is shorter than that for the K321 fibers, indicating that the P-30X fibers are very likely slightly more graphitic than the K321 fibers for the same graphitization conditions. It is also apparent from Table 1 that the SRG reinforcement and its composites are extremely graphitic materials. One other important item from Table 1 is that composite graphitization is shown to be more extensive than that of the fiber alone. This indicates that the matrix will be highly graphitized and therefore contribute substantially to the composite thermal conductivity.

## Results and Discussion

The composite $L_a$ values were used in a rule of mixtures approach to back calculate matrix $L_a$ values using the measured fiber $L_a$, obtained directly from the witness fabric inserted in the graph furnace or from the earlier measurements on SRG [1]. The relationship of mean free phonon path length to coherent crystallite domain lengths, obtained previously for Amoco's high modulus pitch-based (P-55, P-75, P-100) fibers, was used as an initial estimate to calculate mean free phonon path lengths for the P-30X fibers and matrices in these composites. Submicromechanical models [2,3] utilizing Kelly's graphite crystallite conductivity algorithm [4] based on phonon mean free path lengths, were then used to calculate the thermal conductivities of the P-30X fibers and the pitch-based matrix in a pore free state. By treating matrix porosity as cylindrical voids, values for the effective axial and transverse thermal conductivity of the matrix were obtained. Then using measured P-30X composite data, the P-30X fiber and matrix conductivities were adjusted in proportion to their measured $L_a$ values. This process allowed better crystallite domain length to phonon mean free path length relationships to be established for the matrix and P-30X fibers in this study.

With respect to the K321 composites, the pore free matrix conductivity was calculated using the domain length to mean free path length relationship established from the P-30X composites. The measured composite density data was subsequently used to compute the in-situ matrix conductivities by treating the pores as cylindrical voids. It should be noted that, using the measured data and the micromechanical models, a significantly smaller mean free path length exists in K321 fibers than in P-30X fibers for the same graphitization conditions. Consequently, P-30X fibers are apparently capable of achieving higher thermal conductivity than K321 fibers subjected to the same graphitization temperatures.

The degree of correlation between the measured and calculated P-30X composite conductivities is shown by means of the nondimensionalized data plotted in Figure 1. A similar level of correspondence is obtained for the K321 C-C, as indicated in Figure 2.

The calculation of SRG/carbon composite conductivities was performed by means of the same approach described above. The back calculated matrix $L_a$ value is substantially greater for the +,- 2.5° SRG/carbon composites than it is for either of the 0/90 fabric reinforced C-C. This indicates the high level of matrix graphitization achieved when the graphitic layer planes are allowed to fill the columnar regions between the relatively well aligned SRG fibers. The correlation of model calculations with measured conductivities is shown in Figure 3 for the SRG/carbon composites.

## Conclusions

Measured XRD data on C-C composites and on witness reinforcement has provided valuable data for determining the relative participation of the C-C constituents in the composite properties. In the case of thermal conductivity, the matrix values are nearly as significant as those of the matrix. The XRD has proven to be indispensable in the calculation of the C-C constituent conductivities. The validity of the models has been demonstrated by the correlation of calculated and measured conductivities.

## References


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3. B.W. Rosen and B.J. Sullivan, Extended Abstracts, 19th Biennial Conf. Carbon, 1989, pp. 300-301.
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Figure 1.

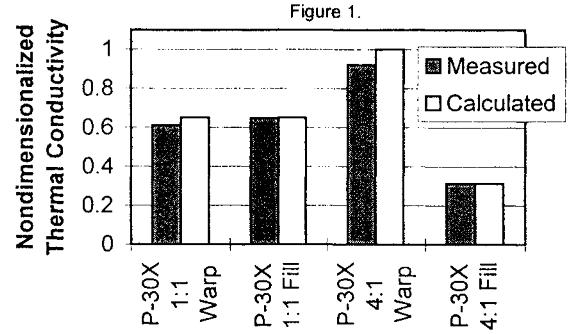


Figure 2.

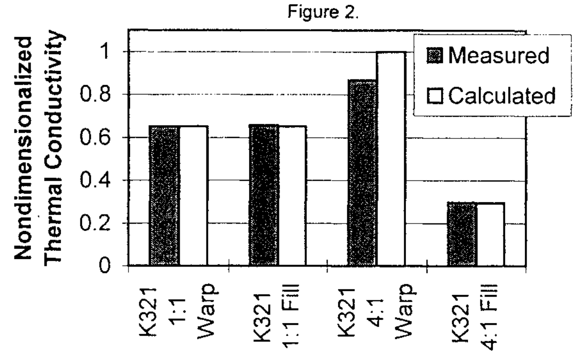


Figure 3.