Properties of Graphite Fiber Reinforced Copper Matrix Composites for Space Power Applications

David L. Ellis
Case Western Reserve University
Cleveland, Ohio

(NASA-CR-191026) PROPERTIES OF GRAPHITE FIBER REINFORCED COPPER MATRIX COMPOSITES FOR SPACE POWER APPLICATIONS Final Report (Case Western Reserve Univ.) 14 p

Prepared for
Lewis Research Center
Under Contract NCC3–94

NASA
National Aeronautics and Space Administration
Properties of Graphite Fiber Reinforced Copper Matrix Composites for Space Power Applications

Dr. David L. Ellis*
NASA Lewis Research Center
Cleveland, Ohio 44135

Abstract

The thermal and mechanical properties of pitch-based graphite fiber reinforced copper matrix (Gr/Cu) composites usable for space applications such as radiator fins were investigated. Thermal conductivity was measured as a function of fiber volume fraction and architecture. Results showed for unidirectional P-100 Gr/Cu composites, the longitudinal thermal conductivity was nearly independent of fiber volume fraction. Transverse thermal conductivities (perpendicular to the fibers) were strongly affected by the fiber volume fraction with higher volume fractions resulting in lower thermal conductivities. The effect of architecture on thermal conductivity followed the cosine squared law for simple architectures. Insufficient data are available currently to model more complex architectures, but adding fibers in the direction of the heat flow increases the thermal conductivity as low conductivity plies are supplemented by high conductivity plies. Thermal expansion tests were conducted on the Gr fibers and Gr/Cu composites. The results show a considerable thermal expansion mismatch between the fibers and the Cu matrix. The longitudinal thermal expansion showed a strong dependence on the architecture of the Gr/Cu composites. The composites also show a thermal expansion hysteresis. The hysteresis was eliminated by an engineered interface. Mechanical testing concentrated on the dynamic modulus and strength of the composites. The dynamic modulus of the Gr/Cu composites was 305 GPa up to 400°C, a value equivalent to Be. The strengths of the composites were less than expected, but this is attributed to the poor bond across the interface between the Gr fibers and Cu matrix. Testing of composites with an engineered interface is expected to yield strengths nearer the values predicted by the rule of mixtures.

Introduction

Space power applications such as radiator fins require materials with high thermal conductivity, low density, and good stiffness. In applications such as the SP-100 nuclear power system, the mass of the radiators may be as much as 90% of the total mass of the power system. Because of this it is desirable to develop materials that can significantly reduce the weight of the radiators. Analysis\(^1\) has shown that the total weight of the radiator system can be decreased by using high thermal conductivity materials for the radiator fins. Comparing graphite fiber reinforced copper matrix (Gr/Cu) composites to beryllium (Be), weight savings of up to 6% can be realized by using Gr/Cu composites. Equal or greater weight savings can be achieved when Gr/Cu composites are substituted for other currently used radiator fin materials. Other advantages include the ability to tailor the thermal conductivity, thermal expansion, and strength of the Gr/Cu composites to match the requirements of the application.

Research is ongoing at NASA Lewis Research Center to develop Gr/Cu composites for use in spacecraft thermal management systems. Preliminary results for the thermal and mechanical properties obtained to date are presented.

Experimental Procedure

Two methods were used for the production of Gr/Cu composites; HIPing copper coated P-100 graphite fibers and pressure infiltration casting of copper and copper alloys into a graphite fiber preform. Most samples made to date have been produced using copper coated graphite fibers. These composites were selected as the initial baseline due to the ease of producing samples with a well defined architecture and no porosity. Newer composites are being produced using the pressure infiltration casting technique so that an engineered interface can be introduced into the Gr/Cu composites.
The samples produced from the copper coated graphite fibers were made at NASA Lewis Research Center using the NASA developed arc spray process. Copper coated P-100 graphite fibers were purchased from American Cyanamid as 2,000 fiber tows. Each individual fiber was coated with a layer of copper using a proprietary process. The thickness of the coating layer determined the volume fraction of graphite fibers in the final composite. The fiber tows were cleaned by passing the tows through a series of cleaning baths to remove surface contamination and wound onto a drum. A thin layer of copper was arc sprayed onto the fibers to produce easily handleable monotapes. The monotapes were laid up into the desired architecture and hot isostatic pressed (HIPed).

A series of 8.9 cm x 6.4 cm x 0.15 cm (3.5" x 2.5" x 0.060") plates with the desired fiber architecture were made for tensile and thermal expansion samples. Four to eight layers of monotapes were used to produce the plates. Tensile test samples 6.4 cm x 1.3 cm (2.5" x 0.5") and thermal expansion samples 2.5 cm x 0.6 cm (1" x 0.25") were machined from the plates. Samples were taken in both the longitudinal (length) and long transverse (width) directions.

A sample 1.3 cm square x 0.5 cm (0.5" square x 0.2") was required for thermal diffusivity testing. A 3.8 cm x 2.5 cm x 1.3 cm (1.5" x 1" x 0.5") block was produced by HIPing 80 to 120 monotapes. The architecture of the blocks followed the pattern of the equivalent plates with the architecture of the plates repeated as often as was required to produce the desired thickness. Samples were taken for all three principal directions. An additional sample 0.6 cm dia. x 0.2 cm thick (0.25" dia. x 0.06" thick) was taken from the block for determining the heat capacity by differential scanning calorimetry (DSC).

The newer technique of producing Gr/Cu composites involves pressure infiltration casting copper or a copper alloy into a graphite fiber preform. The method used was reported elsewhere. The primary advantages of the technique are greater economy in producing the composites, the ability to produce complex near-net/net shaped parts, and the easy ability to introduce an engineered interface. The interface can be produced by using an alloyed matrix that reacts with the graphite fiber to form a thin carbide layer at the interface or by CVD coating the fibers to produce a thin metallic or carbide layer at the interface prior to infiltrating with copper. Using an alloyed matrix is cheaper, but can degrade the transverse thermal conductivities. The CVD coating of the fibers is expensive, but gives better control over the interface. Comparisons between the two techniques are ongoing. The samples were cast by P Cast Equipment Corporation under contract to NASA Lewis Research Center. Plates up to 7.6 cm X 15.2 cm X 0.1 cm (3" X 6" X 0.060") and bars 1.3 cm square by 15.2 cm long (0.5" square X 6" long) have been successfully produced using this method. Longitudinal thermal expansion samples 2.5 cm (1") long taken from the bars have been tested.

Thermal conductivity tests were conducted at the Thermophysical Properties Research Laboratory at Purdue University using the laser flash technique. The heat capacities, \( C_p \), of the samples from room temperature to 800°C were determined using DSC. The room temperature bulk density of the composites, \( \rho \), was measured for the sample before determining the thermal diffusivity, \( \kappa \), of the samples between room temperature and 800°C. From the measured data, the thermal conductivity, \( \lambda \), of each sample was calculated using the equation:

\[
\lambda = \kappa \rho C_p
\]

Thermal expansion testing of the composites was conducted at the NASA Lewis Research Center over the temperature range of room temperature to approximately 825°C using an Orton Model 1600D dilatometer.

Room temperature tensile testing of the composite plates also was conducted at NASA Lewis Research Center. Tensile test samples were wire EDMed from the plates. Steel tabs were affixed to the ends of the samples using epoxy. The samples were tensile tested in an Instron® load frame equipped with MTS® hydraulic grips. An extensometer was used for accurate measurement of the elongation. Load and elongation were recorded by a computer and converted into stress-strain curves after the tests. Following the tensile test, the fracture surfaces were examined in a SEM.
RESULTS AND DISCUSSION

Before presenting the results, it is important to define the terminology with regards to the architectures that will be used in the paper. Figure 1 shows typical unidirectional and angle-plied composites. In all cases, the short transverse direction is perpendicular to the plane of the plate. For both the unidirectional and angle-plied plates, the fibers are perpendicular to the short transverse direction. The long transverse direction is the width of the plate and is defined as the 90° direction. For the unidirectional composites, the fibers are perpendicular to the long transverse direction. The longitudinal direction is the length of the plate and is defined as the 0° direction. For the unidirectional composites, the fibers are parallel to the longitudinal direction.

The angles referred to in the description of the angle-plied composite refer to the angle between the length of the plate and the fibers. For angle-plied plates given a designation with only one number, i.e., ±15°, the plates are made from alternating positively and negatively angled plies mirrored about the center plane of the plate. For angle-plied composites given a three number designation, i.e., +15°/-15°/0°, each number refers to the angle made by the plies. The sequence goes from the surface to the center of the plate. The sequence then mirrored about the center plane of the plate to complete the lay-up of the composite.

![Figure 1 - Designation of principal directions and angles for Gr/Cu composites.](image)

**Thermal Conductivity**

Both architecture and volume fraction of P-100 Gr fibers affect the thermal conductivity of Gr/Cu composites. Figure 2 shows the effect of the volume fraction of Gr fibers on thermal conductivity as a function of temperature for unidirectional composites. Because the longitudinal thermal conductivity of the P-100 Gr fibers is close to that of Cu, the longitudinal thermal conductivity of the Gr/Cu composites is nearly independent of volume fraction of Gr fibers, and the values fall in a narrow band. On the other hand, transverse thermal conductivities are highly dependent on the fiber volume fraction because the fiber has a near zero transverse thermal conductivity. The heat must therefore be carried almost exclusively by the copper matrix. Increasing the fiber volume fraction increases the tortuosity and length of the path the heat must travel through the composite. As a result, the thermal diffusivity and hence the thermal conductivity of the composite decreases as predicted by Eq. 1.

By angle-plying the Gr/Cu composites, the thermal conductivity should be controllable. The longitudinal and long transverse thermal conductivities of the unidirectional and angle-plied Gr/Cu composites as a function of architecture are presented in Figure 3. The thermal conductivity in the longitudinal direction decreases as the
angle of the fibers increases. On the other hand, the long transverse thermal conductivity increases with increasing angle. The thermal conductivities in the short transverse direction were measured for all fiber architectures. The values ranged from 80 to 120 W/mK. The differences in thermal conductivity were attributed to minor variations in the volume fraction of fibers in the composites.

The prediction of the thermal conductivity of Gr/Cu composites is necessary for designing radiator fins and other high heat flux structures. The thermal conductivities of the angle-plied composites were calculated using the cosine squared law:

$$\kappa_C = \kappa_p \cos^2\theta + \kappa_N \sin^2\theta$$  \[2\]

where $\kappa_C$ is the longitudinal conductivity of the angle-plied composite, $\kappa_p$ is the conductivity of a unidirectional composite parallel to the fibers, $\kappa_N$ is the conductivity of a unidirectional composite perpendicular to the fibers, and $\theta$ is the angle between the temperature gradient and the fiber direction. In these samples, the temperature gradient is parallel to the longitudinal direction. A comparison of the predicted and actual values is presented in Figure 4.

![Figure 2 - Effect of volume fraction and temperature on the longitudinal and long transverse thermal conductivity of P-100 Gr/Cu composites. Longitudinal values for composites were in the range bounded by longitudinal low and longitudinal high.](image)

There is good agreement between the predicted and actual values for the composites. The samples for the $\pm 15^\circ$ and $\pm 75^\circ$ samples showed misalignment of the fibers, i.e., the angles of the fibers varying from ply to ply and fibers within the plies not being parallel, than the other samples. This is the reason the samples had the greatest deviation from the predicted values. The test is being repeated with a new sample with better fiber alignment and the desired angle for the plies. It is expected that the results will show a much better agreement with the predicted values. Based on the results for the angle-plied composites, the thermal conductivities can be accurately predicted using the model.

Increased thermal conductivity in the longitudinal direction is possible by adding additional plies of fibers oriented in the $0^\circ$ direction. The long transverse thermal conductivity is decreased, but for radiator fin
applications where heat flow is nearly one dimensional, this is not a problem. Partial results for the thermal conductivity of angle-plied composites consisting of two angle-plied layers on each surface and a core of two 0° plies are presented in Figure 5.

The results show better thermal conductivity in the longitudinal direction. The relative improvement is greater with larger fiber angles. The conductivities in the short transverse direction for the composites were not affected by architecture, so they are not presented in Fig. 5. For the +15°/-15°/0° long transverse sample, there was an anomalous increase in the long transverse thermal conductivity. Based on experience, it is felt that this sample was arc sprayed with a heavier Cu coating on the monotapes. This Cu layer allows for easier movement of the heat through the composites, and, as a result, a higher thermal conductivity. The +45°/-45°/0° long transverse sample followed the anticipated trend of lower long transverse thermal conductivities. Efforts are currently underway to model the thermal conductivity of composites with these more complex architectures.

Figure 3 - Longitudinal and long transverse thermal conductivity of angle-plied P-100 Gr/Cu composites.

Thermal Expansion

To minimize the thermally induced stresses at a braze joint, the coefficient of thermal expansion (CTE) for the two parts should be nearly identical. In space power applications, it is anticipated that the Gr/Cu radiator fins will be brazed to chemically pure titanium (CP Ti). Architecture and volume fraction combinations are being sought to match the two materials.
Figure 4 - Comparison between predicted and measured thermal conductivities of angle-plied 50 v/o P-100 Gr/Cu composites.

Figure 5 - Longitudinal and long transverse thermal conductivities of ±15° and ±45° composites with an inner core of additional P-100 Gr fibers oriented in the 0° direction.
To model the thermal expansions of Gr/Cu composites, the thermal expansion of the constituents must be determined. Data is available in the literature for Cu and Ti. The experimentally determined longitudinal (axial) thermal expansions of pitch- and polyacrylonitrile- (PAN-) based Gr fibers are shown in Figure 6. PAN-based Gr fibers are included as they may be used to improve the transverse strength of the Gr/Cu composites or as fibers for carbon/carbon (C/C) composite radiator fins. The results show the large difference between the longitudinal thermal expansion of Gr fibers and the Cu matrix. However, the thermal expansion of Ti falls between the two materials. It should therefore be possible to match the thermal expansion of Gr/Cu composites to Ti by adjusting architecture and volume fraction.

Figure 7 shows the longitudinal and long transverse thermal expansion of the Gr/Cu composites for a variety of volume fractions. The long transverse thermal expansion of the Gr/Cu composites was greater than Cu and essentially independent of volume fraction. The longitudinal thermal expansion was less than copper and decreased with increasing fiber content. The fibers act to restrain the thermal expansion of the matrix during heating, and greater volume fractions are more effective. Around 50 v/o Gr the composites exhibit a near zero CTE compared to 17 to 20 x 10⁻⁶/°C for Cu. The change in slope seen in the composites with 30 volume percent (v/o) or more Gr fibers is caused by yielding of the matrix due to thermally induced stresses.

The long transverse thermal expansions appear to suggest that the radial thermal expansion of the fibers is greater than Cu. Models examined to date for determining the radial thermal expansion of unidirectionally reinforced composites assume only elastic behavior. Because of the plastic deformation that occurs in these samples, these models are not fully valid. But, an estimate of the radial thermal expansion of P-100 fibers can be made using such a model. For low temperatures, i.e., less than 100°C, the matrix probably has not yielded and the values obtained are reasonable. The values for the thermal expansion of the matrix and composite ($\alpha_M$ and $\alpha_C$), Poisson's ratio for the matrix and fiber ($v_M$ and $v_f$), modulus of the matrix and fiber ($E_M$ and $E_f$) and a packing factor (F) were inserted into Chamberlain's equation.
\[ \alpha_T^C = \alpha_m + \frac{2(\alpha_f^r - \alpha_m)\nu}{\mu_m(F - 1 + \nu_m) + (F + \nu_l) + \frac{E_m}{E_l}(1 - \nu)(F - 1 + \mu_m)} \]  

and the radial thermal expansion of the fibers \( \alpha_f^r \) calculated. The calculated values of the radial CTE of the fibers were between \( 22 \times 10^{-6}/^\circ C \) at \( 100^\circ C \) and \( 50 \times 10^{-6}/^\circ C \) at \( 800^\circ C \), compared to \( 17 \) and \( 20 \times 10^{-6}/^\circ C \) for Cu at the same temperatures. Eliminating the values for the radial CTE obtained when the matrix was clearly undergoing yielding, the radial CTE of P-100 Gr fibers was calculated to be between 20 and \( 24 \times 10^{-6}/^\circ C \). The values are consistent with those obtained for Hercules AS-4 Gr fibers by Gaitonde and Lowson.\(^9\)

Given the large difference in thermal expansion between the long transverse and longitudinal directions, the CTE of the Gr/Cu composites should be matchable to other materials such as Ti by angle-plying. A series of angle-plied architectures are being tested. Results obtained so far are presented in Figure 8. While the longitudinal thermal expansion of a \( \pm 30^\circ \) 50 v/o Gr/Cu composite is significantly greater than that of a unidirectional composite, the value is still less than that of Ti. Evidence of yielding at temperatures between \( 400^\circ C \) and \( 650^\circ C \) was again noted. As expected, the addition of \( 0^\circ \) plies decreased the longitudinal thermal expansion of the Gr/Cu composites. Long transverse thermal expansions should be greater than the longitudinal values presented and closer to the value for Ti.

![Figure 7 - Thermal expansion of unidirectional Gr/Cu composites as a function of volume fraction P-100 Gr fibers.](image)

The thermal expansion of the composites was also measured during cooling. The composites produced by HIPing Cu coated Gr fibers such as the unidirectional 50 v/o P-100 sample shown in Figure 9 all showed a thermal expansion hysteresis. Up to 0.5\% permanent deformation was observed. Figure 9 also shows a sample produced by liquid infiltration casting. The composite with the 0.1 wt.\% Cr addition formed a thin chromium carbide layer at the interface that is highly effective at bonding the matrix to the fiber. Since chromium carbide has an intermediate CTE\(^{10}\) between 7.8 and \( 11.3 \times 10^{-6}/^\circ C \) over the temperature range of interest, it also may act as a compliant layer. The results of having the carbide present at the engineered interface is the elimination of the thermal expansion hysteresis. Samples were also tested that had higher Cr additions or used fibers coated with Ti.
or W that was converted to their respective carbides during pressure infiltration casting. All samples with an engineered interface showed an elimination of the thermal expansion hysteresis.

While most space power applications will not require many thermal cycles, the material will have to be assembled into components, brazed, cleaned, or otherwise heated and cooled a few times prior to entering service. To ensure that the benefits of the engineered interface are not lost due to thermal cycling, samples have been tested up to five cycles from room temperature to 825°C to room temperature. The samples with an engineered interface show no thermal hysteresis for up to five cycles. Composites without an engineered interface have an additional thermal hysteresis with each cycle though the magnitude of the hysteresis decreases with an increasing number of cycles.

![Figure 8 - Longitudinal thermal expansion of angle-plied Gr/Cu composites.](image)

**Figure 8** - Longitudinal thermal expansion of angle-plied Gr/Cu composites.

**Mechanical Properties**

For space power applications, the strength of the composite is not as critical as the modulus. Some dynamic modulus testing was conducted previously, and the results are presented in Figure 10. The dynamic modulus for the Gr/Cu composites is comparable to that of Be (318 MPa) up to 400°C and much higher than Cu. The combination of high modulus and low density of Gr/Cu composites will raise the resonance frequency of the radiator fins to a value much greater than that of the spacecraft.

The room temperature strengths of unidirectional and cross-plied composites are shown in Figure 11 with the value for Cu cold worked 90%. The rule of mixtures,

\[
\sigma_C^L = V_{Cu} \sigma_{Cu} + V_{Gr} \sigma_{Gr} \tag{4}
\]

where \( \sigma_C^L \) is the strength of the composite in the longitudinal direction, \( V_{Cu} \) and \( V_{Gr} \) are the volume fraction of Cu and Gr respectively, and \( \sigma_{Cu} \) and \( \sigma_{Gr} \) are the strength of the matrix and the fibers gives a good estimate of the strength for many composites. For this calculation, residual stresses were ignored, and the value of fully annealed Cu used for \( \sigma_{Cu} \).
Figure 9. Comparison of thermal expansion hysteresis for one thermal cycle for Gr/Cu composites with and without an engineered interface.

Figure 10 - Dynamic modulus of 50 v/o P-100 Gr/Cu and Cu versus temperature.

The longitudinal strength predicted by the rule of mixtures is significantly higher than the values obtained. Examination of the fracture surfaces using SEM (Figure 12) reveals a large amount of fiber pull-out and a very poor bond between the matrix and fiber. Materials with an engineered interface are currently being tested, and the strength of the new composites is expected to be significantly higher since more of the load will be
transferred to the fibers. The transverse strengths of the Gr/Cu composites are also very low due to a lack of a good bond. The strength can be improved by either introducing an engineered interface or using a cross-plied

![Graph showing ultimate tensile strength](image)

**Figure 11** - Ultimate tensile strength of unidirectional and cross-plied 50 v/o P-100 Gr/Cu composites. Values for 90% cold worker (C/W) Cu and the rule of mixtures calculation provided for comparison.

Gr/Cu composite. The improvement in strength for P-100 Gr/Cu composites is shown in Figure 10. While the long transverse strength is increased, the longitudinal strength is decreased due to both a change in fiber architecture and increased fiber breakage during HIPing. An alternate architecture using a few plies of high strength PAN-based Gr fibers running in the long transverse direction with pitch-based fibers running in the longitudinal direction is being investigated as an alternate method of improving the strength of the Gr/Cu composites. For most spacecraft applications, the strength is sufficient at the present levels for use in radiator fins.

**Conclusions**

Gr/Cu composites offer considerable advantages over currently used materials for space power applications. High thermal conductivity, moderate density, and high modulus are combined with the ability to tailor properties to the desired application by proper selection of the composite architecture and graphite fiber volume fraction. Significant weight savings can be achieved by replacing current radiator fin materials with Gr/Cu composites. Ongoing work also has shown that the introduction of an engineered interface by using an alloyed matrix or CVD coating the fibers can eliminate many problems observed in the Gr/Cu composites.
Figure 12 - Fracture surface of Gr/Cu composite without an engineered interface showing considerable fiber pull-out.

References


6 Ibid, pp. 346-347.


# Properties of Graphite Fiber Reinforced Copper Matrix Composites for Space Power Applications

## Abstract

The thermal and mechanical properties of pitch-based graphite fiber reinforced copper matrix (Gr/Cu) composites usable for space applications such as radiator fins were investigated. Thermal conductivity was measured as a function of fiber volume fraction and architecture. Results showed for unidirectional P-100 Gr/Cu composites, the longitudinal thermal conductivity was nearly independent of fiber volume fraction. Transverse thermal conductivities (perpendicular to the fibers) were strongly affected by the fiber volume fraction with higher volume fractions resulting in lower thermal conductivities. The effect of architecture on thermal conductivity followed the cosine squared law for simple architectures. Insufficient data are available currently to model more complex architectures, but adding fibers in the direction of the heat flow increases the thermal conductivity as low conductivity plies are supplemented by high conductivity plies. Thermal expansion tests were conducted on the Gr fibers and Gr/Cu composites. The results show a considerable thermal expansion mismatch between the fibers and the Cu matrix. The longitudinal thermal expansion showed a strong dependence on the architecture of the Gr/Cu composites. The composites also show a thermal expansion hysteresis. The hysteresis was eliminated by an engineered interface. Mechanical testing concentrated on the dynamic modulus and strength of the composites. The dynamic modulus of the Gr/Cu composites was 305 GPa up to 400 °C, a value equivalent to Be. The strengths of the composites were less than expected, but this is attributed to the poor bond across the interface between the Gr fibers and Cu matrix. Testing of composites with an engineered interface is expected to yield strengths nearer the values predicted by the rule of mixtures.