Interfacial Frictional Stresses and Fracture Toughness of Biomorphic Graphite/Copper Interfaces

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Abstract

A fiber push-in test was adapted to measure the interfacial frictional stresses present in wood-derived biomorphic graphite/copper interpenetrating phase composites. Additionally, a sandwich composite was used to measure the interfacial fracture toughness of the copper/graphite system. Results indicate that due to poor wetting of copper on graphite, the surface roughness and extent of mechanical interlocking between the two phases determine the mechanical characteristics of the interface, and that the values are comparable to other metal-ceramic composite systems with limited bonding. A characterization of the mechanically bonded interfaces is vital to understanding load transfer, thermal cycling effects, contact resistance, and thermal conductivity.

Keywords: copper; carbon materials; toughness; interfaces; composite materials

1. Introduction

Bio-inspired and naturally derived materials have garnered recent interest due to their inherently complex microstructures which provide efficient functionality [1, 2]. The porous, honeycomb-like structure of wood-derived ceramics in particular has been exploited for bone implants, catalyst supports, filters, and composite components [3-6]. These materials are produced by converting a wood precursor into a ceramic scaffold; resulting materials exhibit a wide range of microstructures depending on the wood species used, with variations in porosity, pore size and distribution, and connectivity. Various

processing routes, including pyrolyzation, melt/vapor infiltration, and sol-gel techniques, have led to the production of porous carbides, graphite, and oxides [7-11].

Typically, a pyrolyzation process transforms the wood into carbon or graphite and preserves the continuous channels along the axial direction of the tree, as well as the radial and tangential pathways. The fully interconnected network provides a percolated, porous scaffold that can be infiltrated with a second phase to form a composite material. Studies have shown that interpenetrating-phase composites (IPCs) such as these, with complete continuity of both phases throughout the material, allow for the optimization of the greatest number of desirable material properties within a composite system [12].

In the current study, graphite/copper composites are produced from biomorphic graphite (BioG). Graphite/copper composites are of interest as electrical brushes, contact strips, bearing materials, and thermal management materials [13, 14]. These are commonly produced using powder metallurgy techniques, resulting in fiber- or particle-reinforced metal matrix composites [15-18]. By using the natural microstructure of wood-derived graphite as a scaffold for copper infiltration, an IPC can be produced that is mechanically robust and made from an inexpensive, machinable, renewable material. Due to the poor wetting of molten copper to carbon surfaces, the three-dimensional contiguity of the copper and carbon phases provides for mechanical bonding between constituents. Our aim is to investigate the interfacial mechanical properties in this system limited by mechanical bonding.

2. Materials and Methods

Composites were produced by pressure-assisted melt infiltration of a graphitized red oak scaffold, at MMCC, LLC, Waltham, MA. Hardwoods, such as red oak (*Quercus rubra*), have microstructures characterized by long, connected channels (vessels) along the axial direction of the tree which allow the transport of nutrients. During the annual growing cycle, the average diameter of the vessels transitions from larger earlywood channels to smaller latewood channels, resulting in visible growth rings in the cross section of a tree. The red-oak derived BioG scaffold was produced using a pyrolyzation/graphitization treatment catalyzed with nickel nitrate solution as following the procedure outlined in [11]. A cross section of the BioG/Cu composite perpendicular to the elongated channels in the graphitized wood

is imaged in Figure 1. Residual porosity is largely comprised of micron and sub-micron voids located in fibrous regions furthest from the vascular channels, and do not affect interfacial measurements [19].

Composite behavior is dictated by the properties of the constituent materials, their geometry, and their interfacial characteristics. Many composite properties such as strength and toughness are controlled by the bonding between the composite phases. In the absence of chemical bonding at the interface, such as with the poorly wetting copper-graphite system, frictional forces can provide a mechanical link between the two components. For fiber-reinforced composites, a simple method for measuring this force is through use of a fiber push-in test (Figure 2a) developed by Marshall [20]. So long as the specimen thickness is larger than the slipping distance, the resulting interfacial frictional stress, τ , can be approximated from the applied force, the fiber radius and its Young's modulus, and the displacement of the fiber, determined geometrically from the dimensions of the indenter impression sustained by the fiber prior to slip and the indent in the surrounding matrix formed at maximum slip distance when the corners of the indenter contact the matrix material. These mathematical relations are developed fully in [20].

In this work, the fiber push-in test is extended, for the first time, to an IPC, specifically the copper-filled channels of a biomorphic graphite scaffold. The long vessel channels that have been infiltrated with copper offer an analogous testing configuration to that of traditional fiber-reinforced composites. Infiltrated scaffolds were sectioned and mounted in acrylic resin such that the aligned copper channels were perpendicular to the exposed sample face. Samples were polished to a 0.05 μm finish, and a Vickers indenter was used to apply forces between 0.25 and 5 N to the copper channels. Over 20 channels were tested for each sample. The dimensions of the indentations and copper channels were measured using scanning electron microscopy (Hitachi S3400) coupled with image analysis software [21]; ~~any test results~~

that had nonsymmetrical indents were discarded. The most circular channels were chosen for testing, and the channel radii were measured in several directions and averaged to account for any disparities in channel shape. Nano-indentation (Hysitron TriboIndenter) was used to measure the elastic modulus and hardness of the copper in each indent using the method of Oliver and Pharr [22].

Due to the composite morphology in BioG/Cu composites, it is not possible to measure the interfacial fracture toughness (K_{Ic}) directly in the processed material. Therefore, the composite interface was mimicked using a graphite/copper sandwich structure and the interfacial fracture toughness was measured using a single-edge notched bend test, depicted in Figure 2b. As outlined in [23],

$$K_{Ic} = \frac{3Ps\sqrt{a}}{bh^2} \left(1.99 - 2.47 \left(\frac{a}{h} \right) + 12.97 \left(\frac{a}{h} \right)^2 - 23.17 \left(\frac{a}{h} \right)^3 + 24.80 \left(\frac{a}{h} \right)^4 \right)$$

where the parameters are defined in Figure 2b. The sandwich structure was produced using two graphite parallelepipeds, each 35 x 12 x 7 mm³. The graphite contained 8% porosity, ranging from roughly 3 to 100 µm in diameter, and was chosen to adequately mirror the porosity and radial connections on inner channel walls of graphitized scaffolds. The surface was abraded with 120-grit sandpaper to provide roughness similar to that of the graphitized surface in the scaffold. Copper was deposited on the 12 x 7 mm² face of one of the rods using an electrodeposition process similar to those described in [24] and [25]. Rods were plated for 120 hours at 0.3 mA, resulting in a copper thickness of ~0.8 mm. Copper outside sample faces was removed using wire electric discharge machining (EDM). The second, uncoated graphite rod was joined to the copper layer on the first using weld epoxy and set for 24 hours. Right-angle fixtures and clamps were used to ensure alignment and bond strength. After joining, a pre-crack was produced at the copper/graphite interface, using wire EDM, and measured with an optical microscope. Pre-cracks ranged in size from 85-320 µm. The four-point bend test fixture had a span length of 64 mm. The final sandwich specimen geometry and test setup are depicted in Figure 2b.

3. Results and Discussion

Figure 3 shows representative images of indentations. The sample indent was imaged using back-scattered electrons in topography mode to observe the depressed channel and indent dimensions. Copper channels present in the earlywood red oak vessels exhibited the highest interfacial frictional stress of 4.64 ± 2.95 MPa, while those in the latewood red oak vessels had much lower values, 0.17 ± 0.07 MPa. Roughly 20% of all push-in tests were discarded due to asymmetrical indents that were the result of the general non-uniformity of these naturally derived features.

Literature values for interfacial frictional stresses in ceramic fiber-reinforced composites, designed to promote sliding, range from 2-3 MPa for glass ceramic/SiC and glass/SiC composites to 50-80 MPa in Ti/SiC and SiC/SiC composites [26-29]. The values measured in the earlywood channels of BioG/Cu composites have comparable values to the glass/SiC and glass ceramic/SiC systems, known to have negligible bonding, while the interfacial frictional stresses in the latewood channels fall below the reported literature range. During processing of traditional ceramic fiber-reinforced metals, the higher CTE

of the metal compared to the ceramic fiber results in a clamping stress around the fiber during cooling. This results in higher interfacial frictional stresses. In BioG/Cu composites copper acts as the fiber in the long vessel channels and graphite acts as the matrix. As the constituents cool after copper infiltration, the copper phase will shrink more than the surrounding rigid graphite scaffold due to its higher CTE. Therefore, it is not expected for processing-induced clamping stresses to contribute significantly to the measured interfacial frictional stress in these materials.

The large difference between the earlywood and latewood channel values suggests that roughness-induced stresses could affect the observed interfacial frictional stresses in these samples. Pyrolysis of wood preserves many types of inter-vessel structures, such as perforation plates and apertures known as “pits”, which become pathways or recesses for the copper infiltrant. Figure 4 shows a cross section of a graphitized red oak scaffold cut parallel to the elongated channels. The interior of earlywood vessel elements (Figures 4b and 4c) exhibit a high density of circular connecting features (from simple pits), indicated by white arrows, along with regions of larger, elongated pathways (from scalariform pits or perforation plates), indicated by black arrows. Figure 4d shows the interior of a latewood vessel element in graphitized red oak. These channels are characterized by less connectivity and roughness. The circular pits are smaller, and the larger pit features seen in Figures 4b and 4c are absent. Because molten copper does not wet graphite well, all interfacial bonds in these composites are either from physical inter-vessel copper connections or mechanical interlocking at the phase boundaries. As these mechanical interlocks shear, causing the copper “fiber” to slip, the resulting surface roughness from these connections can contribute to higher observed interfacial frictional stresses.[30] Using the maximum coefficient of a Fourier transform of the roughness profile of a fiber, Parthasarathy et al. showed that both increased roughness amplitude and frequency contribute to higher values of interfacial frictional stresses during fiber push-out [31]. Therefore, as observed, the interfacial frictional stresses in the earlywood channels with more porosity and available connections were higher, due to the increased roughness and interconnectivity of the copper fibers.

The interfacial fracture toughness of the copper/graphite system was found to be 0.96 ± 0.35 MPa $\sqrt{\text{m}}$ (or $\Gamma_i = 92 \pm 12$ J/m²). Investigation of fracture surfaces showed that samples with higher toughness values had a higher degree of roughness present at the interface, with small amounts of graphite remaining on the surface of the copper face after fracture. Samples with lower fracture toughness values had smoother interfaces, allowing fewer sites for a graphite/copper engagement, further indicating that mechanical interlocking plays a large role in the interface behavior. Recent studies of the toughness of graphene-copper report $\Gamma_i = 0.34$ to 0.51 J/m², the lower bound for carbon-copper interfaces where no microstructure engagement is expected [32]. This indicates that mechanical interlocking can effectively toughen the carbon-graphite interface by more than two orders of magnitude.

Literature values for interfacial fracture toughness in other ceramic/metal bimaterial systems range from roughly 0.34 - 15 MPa $\sqrt{\text{m}}$ ($\Gamma_i = 2$ to 550 J/m²) [33-36]. Many factors can affect the toughness and debonding mechanism of a system, including interphases or reaction products, layer thicknesses, and mode mixity during testing [37]. The graphite/copper sandwich structure presented no reaction products and exhibited brittle debonding along the interface, as indicated by the lack of metal material attached to the ceramic. The measured toughness of 0.96 MPa $\sqrt{\text{m}}$ is similar to reported values for Al₂O₃-Ni and SiO₂-Cu, both of which also experienced brittle fracture along the interface [34-36]. In contrast, the fracture of Al-Al₂O₃ interfaces transpired largely in the metal phase by microvoid coalescence, and consequently, demonstrated significantly higher toughness values than measured here [33].

4. Conclusions

BioG/Cu composites were produced using red oak-derived graphite scaffolds and pressure-assisted melt infiltration. Interfacial frictional stress and fracture toughness were measured in order to characterize the effects of mechanically bonded interfaces. In both cases, the roughness of the graphite/copper interface was shown to have a large effect. A fiber push-in test was successfully adapted for use on interpenetrating phase composites of copper-infiltrated biomorphic graphite, and showed that the interfacial frictional stress varied between channel type depending on the number and nature of interchannel connections and ranged between 0.17 and 4.64 MPa. A sandwich geometry mimicked the interfaces in the BioG/Cu composite for interfacial fracture toughness measurements. Despite the lack of chemical bonding or interphases, the graphite/copper interface exhibited K_{Ic} values of the same order of magnitude as other ceramic/metal systems due to interfacial roughness.

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Figure Captions

Figure 1: SEM micrograph of a red oak-derived BioG/Cu composite. The alternating bands of latewood (LW) and earlywood (EW) channels are indicated. The composite phase fractions, measured by Archimedes' method, are shown.

Figure 2: Schematic of testing conditions for (a) the “fiber” push-in test, showing cross sections of the displaced copper, indent dimensions, and indenter geometry, used to measure interfacial frictional stresses and (b) the single-edge notched bend test used on an analog sandwich composite to investigate the interfacial fracture toughness of a copper/graphite interface.

Figure 3: Representative copper channels for “fiber” push-in experiments for (a) latewood (LW) and (b) earlywood (EW) features.

Figure 4: SEM micrographs of transverse cross sections of graphitized red oak. Both earlywood (EW) and latewood (LW) channels are visible in (a), while magnified images of the channel walls are shown for (b and c) earlywood and (d) latewood.

Red oak wood

catalytic pyrolyzation

Biomorphic graphite (BioG)

melt infiltration

BioG/Cu composite

Cu-filled fiber-like features with interpenetrating phases through interchannel pathways

Fiber push-out tests

Interfacial frictional stress in infiltrated channels.

Single-edge notched bend tests

Interfacial fracture toughness of analog interface