Composites Science and Technology 89 (2013) 61–68

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Wood-derived copper–graphite composites produced via additive-assisted electrodeposition

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ARTICLE INFO

Article history:
Received 12 October 2012
Received in revised form 4 September 2013
Accepted 11 September 2013
Available online 5 October 2013

Keywords:
Electroplating
A. Functional composites
B. Porosity/Voids
D. Scanning electron microscopy (SEM)

ABSTRACT

An additive-assisted copper electroplating technique designed for infiltrating high-aspect-ratio pores was adapted to work with three-dimensional wood-derived graphitic scaffolds with aspect ratios ranging from 15 to 300. The poor wettability of the carbon/copper system necessitates the development of alternative infiltration techniques to produce composite structures from highly porous precursors such as wood-derived graphite. By incorporating electrolyte additives, copper infiltration was demonstrated into red oak-derived graphite scaffolds, producing a composite with a biologically-derived microstructure. Copper infiltration was studied as a function of electrolyte chemistry and deposition time in two dimensions using electron microscopy techniques and in three dimensions using X-ray computed tomography.

1. Introduction

Composites such as copper/graphite are attractive for their theoretically advantageous thermal and mechanical properties. However, fabrication of these materials, while maintaining control over microstructure, is difficult. Recent work using naturally-derived material systems has illuminated the possibilities of using these materials as a basis for composite design in both thermal and mechanical applications [1–4]. Natural materials, such as wood, can be used as porous precursors which, through pyrolysis and subsequent processing, may be converted into a wide variety of engineering ceramics which retain the naturally-optimized cellular structure of the parent material [5,6]. The wide variety of precursor species with differing open-porous vascular and cellular pore morphologies available combined with the retention of these structures during processing make these biologically-derived materials desirable candidates for composite development [1,7].

In this paper we focus on the development of wood-derived biomorphic graphite/copper composites, building upon techniques applied to biomorphic silicon carbide/copper composites [1,8] combined with recent advancements in production of wood-derived graphite scaffolds [9]. Complications specific to the carbon/copper system, such as poor wettability and significant differences in coefficient of thermal expansion, increase processing complexity, especially when the infiltration of a carbon scaffold with copper is the goal [10–12]. The design advantages associated with using an anisotropically-porous wood-derived biomorphic graphite scaffold in a copper composite structure, however, potentially outweigh these apparent processing difficulties and necessitate the development of an infiltration method.

To avoid the obstacles associated with high temperature melt processing, a copper electrodeposition process has been developed. By careful control of electrolyte additives – plating inhibitors, accelerators, and levelers – copper deposition has been demonstrated into high-aspect-ratio (~10) porosity [13–17]. Plating into the very-high-aspect-ratio porosity found in wood-derived graphite, those with diameter-to-length ratios ranging from 50 to 300 and greater, requires the adaptation of these techniques developed elsewhere. We investigate here the application of electrodeposition to wood-derived graphite and the optimization of electrolyte additives to maximize copper infiltration. The thermal conductivity of resulting copper/graphite composites as well as the porous wood-derived substrate are discussed elsewhere [18].

2. Experimental methods

2.1. Preparation of graphite scaffold

Wood-derived graphite scaffolds were produced from red oak (*Quercus rubra*). Specifics of the graphitization process are covered elsewhere in detail; a brief description is given here [9]. Well-dried red oak samples were vacuum infiltrated with a catalyst solution of 4.25 M nickel (II) nitrate (Alfa Aesar, Wood Hill, MA) and isopropyl

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http://dx.doi.org/10.1016/j.compscitech.2013.09.010

alcohol. After a 5-day immersion in catalyst solution, samples were removed and first dried in air then in a vacuum-assisted drying oven. Graphitization was carried out in a pyrolysis/graphitization heat treatment performed in a nitrogen atmosphere at a maximum temperature of 1600 °C. Residual nickel was removed via a washing process in 37% HCl.

2.2. Processing of graphite/copper composites

The electrolyte solution used was adapted from previous studies, for use specifically with high-aspect-ratio copper microvias and circuit features [13–15]. The Dow et al., electrolyte includes both an accelerator and surface leveler in addition to a polyethylene glycol (PEG) inhibitor. Here, a 0.88 M $CuSO_4$–$5H_2O$ solution is prepared with 0.54 M H_2SO_4, 60 ppm chloride (from HCl) and a balance of deionized water. A fixed addition of 200 ppm 3400 MW PEG is added as an inhibitor. SPS (bis-(3-sulfopropyl)-disulfide, RaluPlate SPS, Raschig GmbH, Ludwigshafen, Germany), an accelerator, and Diazine Black (DB, Sigma–Aldrich, St. Louis, MO), a leveler, are added in concentrations varying from 0 to 1 ppm. The electrolyte solution was stirred thoroughly then samples were added with an oxygen-free high-conductivity (CU101, McMaster-Carr, Elmhurst, IL) cathode. A constant DC current of 10 mA was applied and maintained during the plating process.

To characterize the role of the accelerator and leveler additions, electrolytes were prepared with concentrations of accelerator and leveler varying from 0.00 to 1.00 ppm with a step size of 0.25 ppm, producing a 5×5 sample space. Although additive concentrations are somewhat lower than reported elsewhere in literature, it was determined through an initial series of experiments that this region of concentrations yielded the best plating performance. For each concentration combination, $12 \times 12 \times 3$ mm^3 red oak-derived graphite samples were plated for a period of 120 h in 200 mL of electrolyte and subsequently analyzed.

2.3. Characterization methods

2.3.1. Two-dimensional analysis

The primary method used to evaluate composite microstructure and copper plating performance was two-dimensional image analysis. Following electroplating, composite samples were sectioned to their mid-plane, shown schematically in Fig. 1, using traditional metallography grinding and polishing procedures. Composites were first mounted in epoxy then ground using 320-grit silicon carbide grinding media; thickness was monitored using Vernier calipers until the mid-plane was reached. A final polish was performed using successive passes of 9, 6, 3, and 1 μm diamond polishing suspensions to clean the surface and remove excessive scratching.

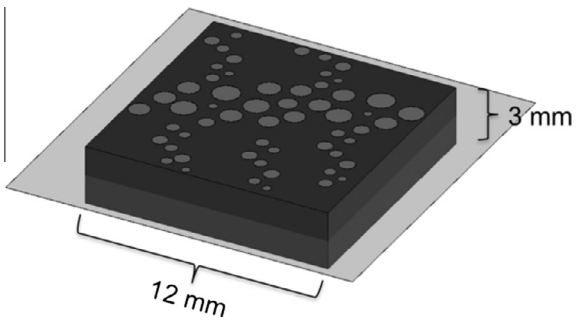

Fig. 1. Schematic of sample cross-section geometry. Microscopy was performed at the mid-plane of a 3 mm thick composite with the porosity axis aligned vertically as shown.

Following surface preparation, micrographs of the polished surface were collected via SEM (Hitachi S-3400-II SEM, Hitachi, Pleasanton, CA). In order to observe contrast of all three phases present, two images were collected of identical sample regions, one using secondary electron (SE) imaging and one using backscattered electron (BSE) imaging. In BSE images, the contrast between copper and carbon phases is strongest whereas in SE mode, residual porosity is easily observed. Fig. 2 shows an example of the relative contrast difference between a BSE image (Fig. 2)) and an SE image (Fig. 2(b)); here, it is important to note the areas of dark residual porosity in the SE image that are less evident in the BSE image. Combining these two images in subsequent image analysis simplifies the image segmentation process to come. Two non-overlapping sets of images, each measuring 4.8×10.3 mm^2 were collected from each sample evaluated, effectively capturing the majority of the roughly 12×12 mm^2 surface area.

To analyze each set of images, first, a posterization process was applied using Adobe Photoshop CS4 software (Adobe Systems, Inc., San Jose, CA) to reduce each grayscale image, consisting of 255 shades of gray, into a grayscale image consisting of 5 shades of gray, thus simplifying thresholding. Regions of copper were obtained by thresholding BSE images while void spaces were acquired by thresholding SE images. These two figures were subsequently overlaid and the balance of the area was taken to represent the graphite matrix. In the example shown in Fig. 3, white regions show areas of copper, black regions show areas of residual porosity, and gray regions represent graphite. Next, using ImageJ, [19] the area fractions of each phase were calculated and the percentage of "available pores" filled was calculated following

$$\%\ \text{Pores filled} = \frac{\text{Area}_{\text{Cu}}}{\text{Area}_{\text{Cu}} + \text{Area}_{\text{Void}}}. \quad (1)$$

In this case, available pores represent those which originate from the parent wood's vascular structure and are therefore connected, through-pores, which may be plated via electrodeposition. Small, cellular pores, with little or no connectivity are omitted as they are inaccessible to the electrolyte. Using this technique allows for sample-to-sample variations, common when using natural sources such as wood, to be normalized.

2.3.2. Three-dimensional analysis

An alternative, non-destructive technique for evaluating porous and composite structures is the use of X-ray computed tomography (XCT) [20,21]. For this work, XCT was performed at the Advanced Photon Source (APS), Beamline 2-BM, Argonne National Laboratory. Graphite and graphite/copper composites measuring 3 mm in diameter and approximately 3 mm in height were machined out of larger plated samples using an ultrasonic drill press fitted with a diamond-composite coring bit. Samples were mounted to XCT stubs using modeling clay. Graphite-only samples were imaged with a 12 mm sample-to-detector working distance at an energy of 23.8 keV and an exposure time of 300 ms. For graphite/copper composites, the working distance and energy were increased to 23 mm and 25.8 keV, respectively, while the exposure time was reduced to 200 ms. In both cases, a Coolsnap K4 CCD camera (Photometrics, Tuscon, AZ) with a 5× microscope objective lens and a 100 μm-thick LuAG:Ce scintillator screen were used to collect 1500 radiographs as samples were rotated through 180°, producing a step-size of 0.12°. The camera uses a 2048×2048 pixel CCD with a physical pixel size of 7.4×7.4 μm^2, yielding an image pixel size of ~1.46 μm/pixel and a field of view of 3 mm^2. Volumetric images were obtained using the Gridrec algorithm [22].

The product of image reconstruction is a series of 2D grayscale images, with lighter shades of gray representing regions with a higher X-ray attenuation coefficient. Copper, with a significantly