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Materials Science and Engineering A 460–461 (2007) 344–350

MATERIALS SCIENCE & ENGINEERING A

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Oxidation of copper fiber surface to improve fracture toughness of Cu/epoxy composite

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Received 19 June 2006; received in revised form 15 January 2007; accepted 18 January 2007

Abstract

Controlled oxidation treatments are applied for the first time to the surface of ductile Cu fibers which are used in epoxy matrix composites. The oxidation treatments produce either "A-nanoleaves" or black or red oxide "B-nanoleaves" with various nanoscale morphologies. Single fiber pullout (SFP) tests were performed on the oxidized fibers to evaluate how friction produced by their engineered surfaces will affect composite toughness. A highly cross-linked epoxy (HCLE) showed excellent formation of individual asperities which provided a significant increase in pullout work with black oxide B-nanoleaves. A standard epoxy (SE) with lesser cross-linking showed no asperities but rather a general roughness which also produced a significant increase in pullout work with black oxide B-nanoleaves. It was found that the standard acetone pre-treatment which is applied to remove polar impurities before oxidation can be shortened substantially from the standard 20 min to 5 min.

Keywords: Ductile fibers; Fracture toughness; Composites; Surface oxidation

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1. Introduction

If a brittle matrix is reinforced with metal fibers, the resulting composite has good toughness, stiffness, strength, and hence reliability [1]. Ductile metal fibers such as copper have a large plastic work potential which can contribute to composite toughness if properly utilized. This potential is absent in most high modulus fibers (e.g. glass), which have little to no plastic deformation and exhibit brittle failure. Another benefit of ductile fibers is that if a fiber is not perpendicular to the crack surface, it can bend as it bridges the crack and still pullout of the matrix. Brittle fibers cannot bend at the crack surface; they tend to break with minimal pullout when misaligned [2].

The addition of copper fibers to a thermoset matrix creates a multifunctional composite with high stiffness, toughness, strength, and EMI shielding [3]. Applications of these composite materials include non-destructive measurement of damage within the composite by monitoring variation in conductivity [4] and applications in machine brake materials since copper fibers exhibit good friction and elevated temperature fade resistance [5]. These composites also find application in deicing surfaces by means of Joule heating, since copper fibers have high electrical conductivity [6]. These composites are also extensively used in microelectronics applications and printed circuit board technology where copper leadframes are embedded in an epoxy matrix [7–14]. However, the important factor in the applications noted above is the control of the adhesion and interaction between epoxy resins and copper fibers or foils. This requires a fundamental understanding of adhesion at copper-based metal/polymer interphases [10].

As-received, pure copper exhibits poor adhesion characteristics for bonding to polymeric substrates. This is because of the presence of native copper oxides on the copper surfaces, which are mechanically weak and hinder wetting of the copper surface by epoxy [11], as well as the presence of organics from the manufacturing process. To improve adhesion between copper foils and an epoxy matrix, the directed oxidation of a cleaned copper surface prior to its coming in contact with epoxy has been used with success [10,11]. Another approach to producing copper oxides has involved plasma treatment of copper surface with flurohydrocarbons [7,8]. In yet another method the copper foils were subjected to high annealing temperature of about 400 °C in presence of oxygen flow (150 ml/min) for extended periods of time [12]. The last two methods are complex and possess

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doi:10.1016/j.msea.2007.01.055

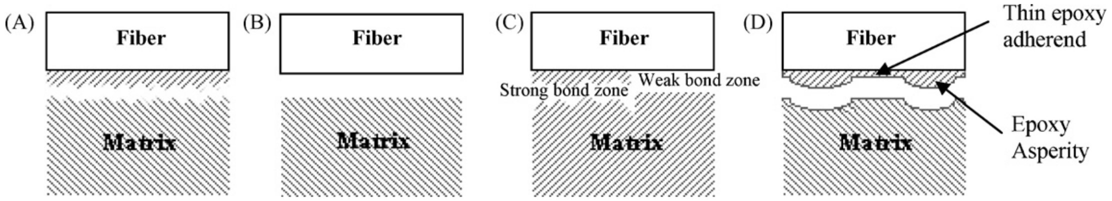

Fig. 1. Schematics of: (A) cohesive bond failure, (B) interfacial bond failure, (C) mixed mode failure (theoretical), and (D) mixed mode failure (as observed).

high energy requirements, however, and are not acceptable for low-cost manufacturing.

Lower cost, simpler alternatives have been created to oxidize Cu foil surfaces. Lee et al. [9], in their paper used two methods of oxidizing treatment on copper foils to form leaf-like nanoscale copper oxide features. They subsequently studied the adhesion strength of these engineered copper foils. For forming these oxide features, they followed the procedures used by Love and Packman [10] which produces features they have termed “A-nanowires”, and the procedures of Yun et al. [11] which produces “B-nanowires”. However, examination of scanning electron microscope (SEM) images from these references and from this work show that this term is somewhat imprecise. The elements of the oxide features are prismatic or flake-like, not wire-like; they had measurable heights and breadths and collectively had a leaf-like appearance. For one of the treatments, the elements are grouped into larger features which are also leaf-like. Hence, the term “nanoleaves” has been introduced in this work, which seems to be a more appropriate description for these nanoscale oxide features and are henceforth called so in this work. A similar term, “nano-belts” has been introduced in recent work by Lee et al. [9], confirming the fact that the oxide features do not appear wire-like.

The oxide features which are grown on the foil are very effective in improving the mode I toughness of the interface because they interlock at a very fine scale with the neighboring epoxy. In this work, the Cu fibers contribute toughness to an epoxy matrix by crack bridging and pullout. Thus, while the composite fracture is mode I, the failure of the Cu–epoxy interphase is in mode II. Previous research has shown that a balance must be struck for the interaction at the interphase in the composite: either a too-strong or too-weak anchoring of the fibers in the matrix will result in poor utilization of the plastic work potential in the fibers and thus in a low composite toughness [1]. The desirable fracture mode is mixed and the epoxy which adheres to the fiber during pullout plays a critical role (see Fig. 1). A proper level of friction can be supplied by roughness of the adhered matrix or by larger asperities found on the surface of the adhered matrix. In this paper, we will determine the required pre-treatment (cleaning) steps, the growth of the oxide features, and the correlation between oxide features and the pullout work of the fiber.

2. Materials and methods

The surface of Cu foils were cleaned (pre-treated) and then oxidized. The foils used are 99.9% pure, conform to ASTM standard B3, and were approximately 12 mm × 25 mm × 0.13 mm thick. Using treatments from the literature for the pre-treatment [9–11,14], the foils were dipped in chloroform for 2 min and then ultrasonically agitated in acetone for 20 min to remove non-polar and polar contaminants, respectively. Finally, the foil was dipped in concentrated hydrochloric acid for 3 min to remove native oxides. In between all steps, the foil was rinsed with distilled water and air dried.

The foils were suspended in the solutions and not permitted to lie down within the container. Oxidation treatments were chosen that produced either “A-nanoleaves” or“B-nanoleaves” [10,11]. A general discussion of the chemistry of oxidation of Cu surfaces using $NaClO_2$ can be found in [15]. For the A-nanoleaves, the oxidizing solution was made up of 160 g/l of $NaClO_2$ and 10 g/l of NaOH as a buffer to maintain a high oxidizing potential [10,21]. Oxidation treatments were carried out both at room temperature (RT) and at $70 \pm 2\,^{\circ}C$. A detailed examination of the surface using X-ray photoelectron spectroscopy (XPS) shows that the oxide features are CuO. Two types of B-nanoleaves were developed: black oxide and red oxide, where the name refers to the color of the oxide formed on the copper foil [11]. For the black oxide B-nanoleaves, the oxidizing solution consisted of 37.5 g/l of $NaClO_2$, 50 g/l of NaOH and 100 g/l of $Na_3PO_4{\cdot}12H_2O$ as buffer. This composition of the solution along with the high temperature of $95 \pm 2\,^{\circ}C$ made the solution quite aggressive. A later paper details the chemistry at the surface [16]. A very fine layer of Cu_2O forms at the surface in the very initial stages and then CuO oxide features grow and dominate the surface after that. For the red oxide B-nanoleaves, the oxidizing solution was much milder, consisting of 37.5 g/l of $NaClO_2$, 6 g/l of NaOH and 25 g/l of $Na_3PO4{\cdot}12H_2O$. The oxidation temperature was maintained at $85 \pm 2\,^{\circ}C$. X-ray photon spectroscopy (XPS) results reveal the red oxide B-nanoleaves to be primarily Cu_2O [21], as expected from their color. After the growth of oxide features was demonstrated on foils, a subset of these oxidation treatments was applied to Cu wires of 0.315 mm diameter which are 99.99% pure and meet ASTM B3 standards.

In addition to qualitatively demonstrating adhesion quality, single fiber pullout (SFP) tests can be used to measure the work required to pull the fiber from the matrix, thus providing a quantitative measurement of the interface behavior. Furthermore, the SFP test can provide a prediction of the fracture toughness contribution of the fibers to the composite. The SFP test is based on work by Piggott and Dai [17], and further extended by Wetherhold et al. [18–20]. The wires were embedded into epoxy matrix at 0° angle and SFP tests were carried out after the matrix had cured for 48 h. Two different epoxy compositions were used in this work. A mixture of Epon® Resin 815C, EpiCure® 3234 curing agent and Cabosil (silica) in the ratio 100 g:30.0 g:3.5 g with increased cross-linking is referred to as “highly cross-