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Electron microscopy and electron-energy-loss spectroscopy study of crack bridging in carbon–carbon composites

B. Reznik *, M. Fotouhi

Laboratory for Electron Microscopy, Karlsruhe University, 76128 Karlsruhe, Germany

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Abstract

Crack bridging within pyrolytic carbon matrix of a carbon-fiber/carbon-matrix composite was studied by scanning electron microscopy and transmission electron microscopy combined with electron-energy-loss spectroscopy. An extensive propagation of concentric cracks around carbon fibers is observed in the matrix. The crack propagation is bridged by bent lamellae. The analysis of low-energy-electron losses in cracked regions shows that the bulk $(\pi + \sigma)$ plasmon of planar lamellae lies close to those of graphite while the bulk $(\pi + \sigma)$ plasmon in bent areas is shifted towards lower energy positions and is comparable with the plasmon resonance of a polymer film. The morphology of bridging areas is discussed by considering the degradation of the atomic structure of planar graphite by the presence of lattice defects and hydrogen atoms.

Keywords: A. Carbon–carbon composites; C. Crack; D. Scanning electron microscopy; Transmission electron microscopy; Electron-energy-loss spectroscopy

1. Introduction

The production of high-performance components such as break assemblies, flywheels, filament wound pressure vessels requires materials exhibiting superior mechanical properties like high fracture toughness, low notch sensitivity and high strength/weight-ratio. Carbon-fiber/carbon-matrix (C/C) composites produced by chemical vapour infiltration (CVI) of carbon fiber felts are potential advanced materials for such applications [1]. The mechanical properties of composites, in particular the composite toughness is frequently associated with arrest of propagating matrix cracks by carbon fibers [1–3]. Using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), Reznik and Gerthsen [4] observed different cooperative failure mechanisms within the pyrolytic carbon matrix including crack deflection in interface regions between layers with different texture degree, crack deflection along boundaries of columnar grains and crack bridging within high-textured lamellae [4]. Among them, the crack bridging is a particular failure mechanism, which however has not been studied in details.

It is well-known that crack bridging is an important failure mechanism contributing to the toughness enhancement of different composite materials [1–3]. Thus, the basic understanding of the crack bridging mechanism is important and can provide a means of significant improvement of the fatigue performance of C/C-composites.

The present contribution aims to answer the question regarding the bonding state of carbon atoms (σ- and π-states in graphitic carbon) within cracked regions as compared to the undisturbed matrix. Bonding states are accessible by electron-energy-loss spectroscopy (EELS) in a transmission electron microscope which can be carried out with high spatial resolution through (a) plasmon loss spectra (low energy loss region up to about 50 eV) originating from the collective excitation of valence electrons and (b) the high-energy loss region (around 284 eV) containing

* Corresponding author. Tel.: +49 0721 608 3720; fax: +49 0721 608 3721.
E-mail address: reznik@lem.uni-karlsruhe.de (B. Reznik).

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information about the inner shell ionizations [5]. In particular, two plasmon peaks related to the excitation of π and π + σ electrons are used for the analysis of the carbon bonding state. It allows a clear distinction of diamond- and graphite-like materials with different crystallization degrees [6]. Plasmon energy values are closely related to physical properties of graphite-like materials [7–9]. Therefore, in the present work, the crack bridging mechanism is studied by analytical TEM coupled with EELS in the low-loss region and by combining high-resolution SEM and TEM.

2. Experimental

The C/C-composites were fabricated by chemical vapour infiltration (CVI) of a carbon fiber felt which is in detail outlined by Benzinger and Hüttinger [10]. Briefly, the infiltration of the fiber felts was performed at a temperature of 1100 °C in a hot-wall reactor using a gas mixture consisting of CH_4 and H_2 with a partial pressure ratio of 7:1 at a total pressure of 20 kPa. The total size of the composite was $20 \times 20 \times 35$ mm^3.

A 3 mm disk was cut from the central part of the composite with an ultrasonic cutter which was used for the TEM sample preparation. The remaining piece of the composite was used to obtain fracture surfaces for the SEM studies as described elsewhere [4]. Freshly fractured surfaces were examined by SEM in a LEO 1530 microscope with a Schottky field-emission gun without evaporating conductive layers prior to the investigation. For the TEM specimen preparation, slices with a thickness of 200 μm were cut from the composite and further reduced in thickness by mechanical grinding and polishing to 80 μm. The obtained foils were carefully dimpled down to a few micron thickness or even to perforation using diamond polishing pastes. Two argon-ion guns operating at 1 kV, a current of 1 mA under an angle of ±4° were used for a few minutes for the final removing of residual paste from foil edges. No material amorphization or debris removing have been detected under these cleaning conditions.

The TEM was carried out in a LEO EM 912 Omega transmission electron microscope at electron energy of 120 keV, which is equipped with an Omega electron-energy spectrometer integrated into the projection lens system. This analytical microscope allowed obtaining information regarding the type of chemical bonding using EELS by acquiring of low-energy losses. EELS spectra were taken with a spot size of 10 nm which provides a good spatial resolution within cracked regions. The spectra were acquired with a 1024×1024 pixel charge-coupled-device (CCD) camera with an exposure time of typically 50 ms. Amorphization or structure changes were not observed under the applied illumination conditions. Polycrystalline natural graphite and holey formvar film, i.e. a polymer film, were used as reference materials. The high-resolution TEM was carried out in a Philips CM 200 FEG/ST electron microscope operated at 200 kV. The instrument is characterized by a Scherzer resolution of 0.24 nm and an information limit of 0.15 nm.

3. Results

Representative SEM micrographs of a freshly fractured composites are presented in Fig. 1. Concentric microcracking within the pyrolytic carbon matrix around differently tilted carbon fibers is evident (Fig. 1a). The cracks follow the layers around fibres rather than going through the pyrolytic carbon matrix. The propagation of concentric cracks is arrested by bridging lamellae (s. the arrows in Fig. 1b). The bridging lamellae are distributed randomly along concentric cracks; its relative concentration is about 10%.

Fig. 2 displays crack bridging structures observed in thin TEM foils. The revealed crack morphology and its bridging are similar (Fig. 2a) to those found by SEM (Fig. 1b). Fig. 2b displays a high-resolution TEM image of a region containing a crack which propagation is stopped by the bridging lamellae. As illustrated by the inset, the planar lamellae consist of turbostratic stacks of graphene planes. In contrast, the bridging, bent lamella contains curved graphene planes (arrow).

The collected EELS spectra are presented in Fig. 3. The spectrum of graphite (curve 2, Fig. 3a) contains two prominent characteristic plasmon excitations at about 6 eV (π peak in (a)) corresponding to $\pi \rightarrow \pi^*$-transition and at ~27 eV (π + σ peak in (a)) corresponding to the bulk (π + σ) plasmon. In contrast, the spectrum of the polymer film contains only a π + σ peak shifted to ~22 eV (curve 1, Fig. 3a). Therefore the results presented here are focused mainly on the energy value for the π + σ peak. The spectra from cracked regions are based on the results presented in Fig. 3b. The spectrum from the planar lamella (curve 4, Fig. 3a) is similar to the graphite spectrum (curve 2, Fig. 3a). The EELS from the bent lamella (curve 3, Fig. 3a) shows a systematic shift of the π + σ peak position towards lower energy in comparison with the planar lamella (Fig. 3b). Besides, the π peak is weaker (curve 3, Fig. 3a).

4. Discussion

Crack bridging of concentric cracks within the pyrolytic carbon matrix of an infiltrated carbon fiber felt is observed by SEM and TEM. The crack bridging occurs by bent lamellae along paths of concentric cracks. Energetic positions of the bulk plasmon excitations in EELS spectra indicate that the material of bent lamellae is comparable with a polymer film while the crack-free planar lamellae are similar to graphite.

An intensive propagation of concentric matrix cracks in pyrolytic carbon matrices is observed by SEM (Fig. 1). The cracks follow the concentric layers around fibers rather than going through the matrix and show no prominent dependence on the fracture direction [4]. These observa-