

STRUCTURE AND PROPERTIES OF PYROLYTIC CARBON: RECENT DEVELOPMENTS AND HIDDEN POTENTIALS

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Abstract

Recent developments on the relationship between the complex microstructure of pyrolytic carbon coatings and the pyrolysis conditions are reviewed. Pyrolytic carbon coatings deposited on carbon fibers and non-carbon substrates are studied comparatively by light microscopy, scanning electron microscopy and transmission electron microscopy combined with selected-area electron diffraction. Optically uniform coatings exhibit pronounced gradual changes in texture degree of graphitic crystallites at the sub-micrometer-scale if investigated by electron diffraction. The thickness of the reaction layer at the pyrolytic carbon /carbon fiber interface depends on the carbon fiber crystallization degree. The porosity of coatings is influenced by the reactor cooling rate. All these studies suggest a large potential of pyrolytic carbon for the design of multifunctional coating materials.

Keywords: Carbon composites, Chemical vapour infiltration, Pyrolytic carbon

Introduction

It becomes increasingly important to obtain a better fundamental understanding of the physics and chemistry of the chemical vapor deposition/infiltration process (Oberlin, 2002). A great deal of effort has been expended in recent 8 years at the University of Karlsruhe relating the complex microstructure of pyrolytic carbon coatings to the pyrolysis conditions (Guellali et al, 2003; Hu et al, 2003; Zhang and Hüttinger, 2001) as well as to the mechanical properties of carbon-carbon composites with pyrolytic carbon matrices (Piat and Schnack, 2003; Piat et al, 2003). In order to reveal possible potential implications of pyrolytic carbon coatings, the present contribution discusses the recently studied microstructural features of pyrolytic carbon coatings including textural gradients (Reznik et al, 2003a; Chen et al, 2005), high-textured reaction layers at substrate surfaces (Reznik and Gerthsen, 2003; Gerthsen et al, 2006) and surface-located nanopores (Reznik et al, 2006).

Results and discussion

Textural gradients

The formation of textural gradients under the constant chemical vapor infiltration conditions is illustrated in Figs 1 and 2. The upper of Fig.2 shows polarized light micrographs (PLM) of infiltrated carbon fiber felts prepared as foils for transmission electron microscope. Carbon fibers are embedded in pyrolytic carbon matrices exhibiting different contrast due to the different global optical textures (Reznik et al, 2003a). A textural gradient at the sub- μm -scale is determined by selected-area electron diffraction (SAED) (Reznik et al, 2003a; Chen et al, 2005). For this purpose a SAED aperture is positioned close to the fiber surface and moved into the matrix with steps equal to its diameter along the white dotted lines shown in PLM micrographs (Fig.2). The texture degree is characterized by measuring the full width at half maximum (FWHM) intensity of the azimuthal opening of (002) reflections (Fig.1a), and is denoted as orientation angle OA (Fig. 1b). Certain ranges of OA values (Fig.1c) can be assigned to high-textured, medium-textured and low-textured alignment of graphitic planes with respect to the substrate (fiber) surface (Reznik and Hüttinger, 2002).

The SAED data (Fig.2, bottom) illustrate clearly that optically uniform matrix areas exhibit pronounced changes in texture degree of graphitic crystallites at the sub-micron scale. The textural changes correlate with changes of the deposition partial pressure of methane - the highest total texture degree and the smallest texture gradient are achieved at an intermediate infiltration pressure (Fig.2b) (Reznik et al, 2003a).

High-textured reaction surface layers

As the structural and chemical properties of the interface determines the adhesion between fiber and matrix, the control of these properties is highly desirable to optimize the mechanical characteristics of the composite and to minimize failure of the material. Fig. 3 illustrates the formation of a high-textured reaction layer at the surfaces of carbon fibers studied by high-resolution transmission electron microscopy (Gerthsen et al, 2006). In the case of the high-tenacity fiber (Fig.3a), the reaction layer is less than 20 nm. A layer up to 100 nm thick is observed at the surface of high-modulus fibers (Gerthsen et al, 2006). Similar reaction layers are also observed on non-carbon substrates like e.g. cordierite (Gerthsen et al, 2006). The stress-induced ordering due to the thermal stresses (Hishiyama et al, 1974) generated during the reactor cooling is discussed as a mechanism for the formation of the high-textured interface layers. The different coefficients of thermal expansion of the matrix and

carbon fiber, especially high-modulus fibers with a higher crystallization degree provoke these stresses. Moreover, dehydrogenation of pyrolytic carbon can lead to the shrinkage of the graphene layers and tensile stresses (Gerthsen et al, 2006).

Nanopores

The formation of nanopores correlating with hydrogen release in pyrolytic carbon coatings during the reactor cooling is shown recently (Reznik et al, 2006). High-resolution scanning electron microscopy (HRSEM) observations (Fig. 4) demonstrate that the increased cooling correlates with a decreased density of pores in the uppermost part of coatings, i.e. the coating porosity can be controlled by the reactor cooling rate.

Structural concepts of pyrolytic carbon coatings

The found microscopical data indicate an extremely high ability of pyrolytic carbon to take differently textured forms and to exhibit different porosity degree. This material exhibits properties which cannot be easily generated in common functional materials (Hirai, 1996). However, at present there is no reliable coating technology allowing to control of the texture and architecture of pyrolytic carbon coatings. For example, the deposition of graded, multilayered and nanoporous/textured coatings (Fig.5) can open the way towards improvement of e.g., thermal expansion, thermal conductivity, shock resistance and fracture toughness of carbon/carbon composites. Additionally, the nanoporous coatings can be also utilized in sorption applications (Inagaki, 2000). Therefore, the exploiting the property potential of pyrolytic carbon is a challenge for the research and development community.

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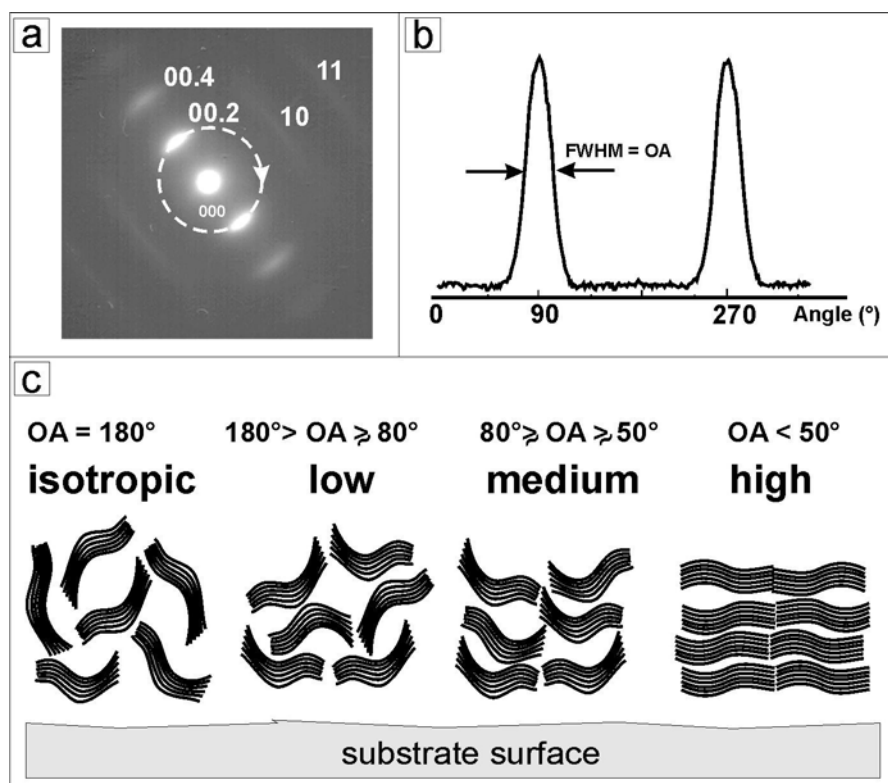


Figure 1. (a) Electron diffraction pattern with dashed circle indicating the direction the azimuthal intensity scan, (b) The extracted intensity distribution, (c) Correlation between OA values and types of coating textures (Reznik and Hüttinger, 2002).

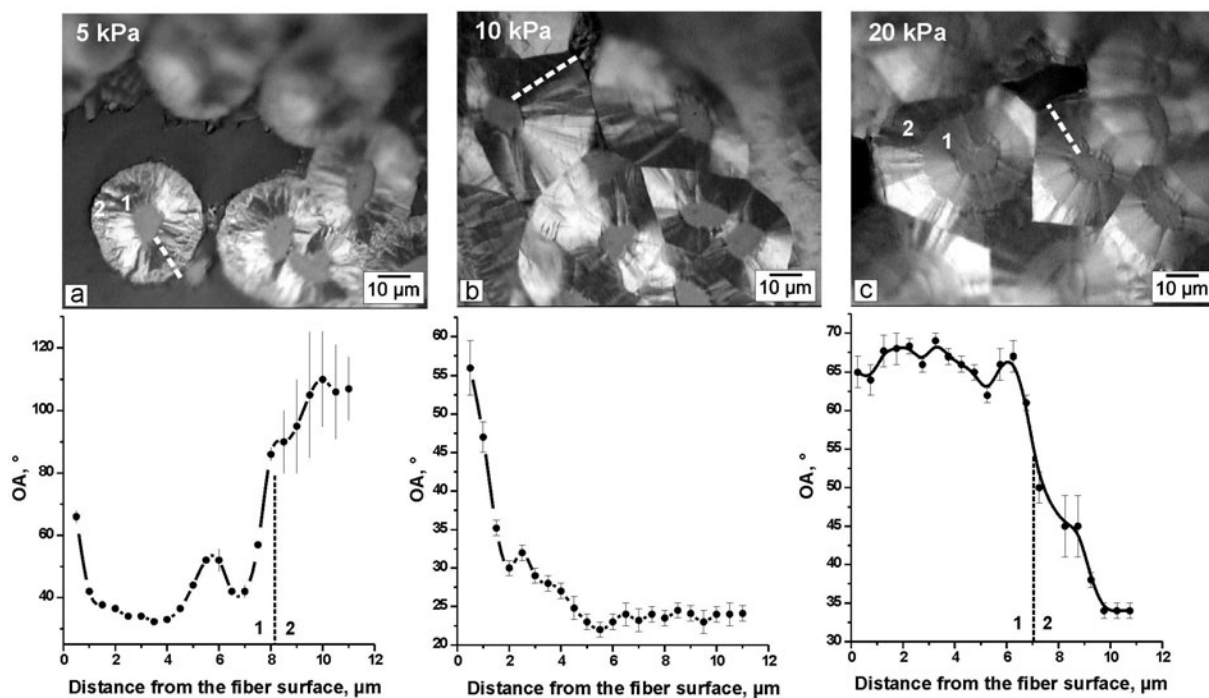


Figure 2. PLM micrographs (top) of thin foils of infiltrated carbon fiber felts and texture plots (bottom) obtained along the dotted lines. The felts have been infiltrated from methane at partial pressure of 5(a), 10 (b) and 20 kPa (c) at 1095 °C (Reznik et al, 2003a).

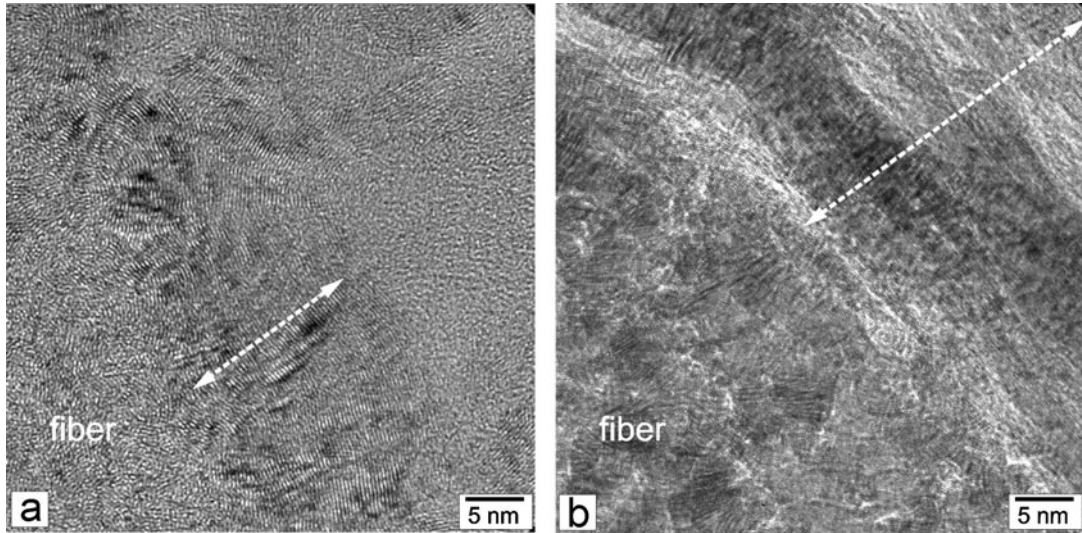


Figure 3. HRTEM images of the fiber-matrix interface of infiltrated unidirectional high-tenacity (a) and high-modulus (b) carbon fiber bundles. The dashed arrows indicate the approximate extension of the high-textured reaction layers. The bundles have been infiltrated for 120h at a temperature of 1100°C and a methane pressure of 20 kPa (Gerthsen et al, 2006).

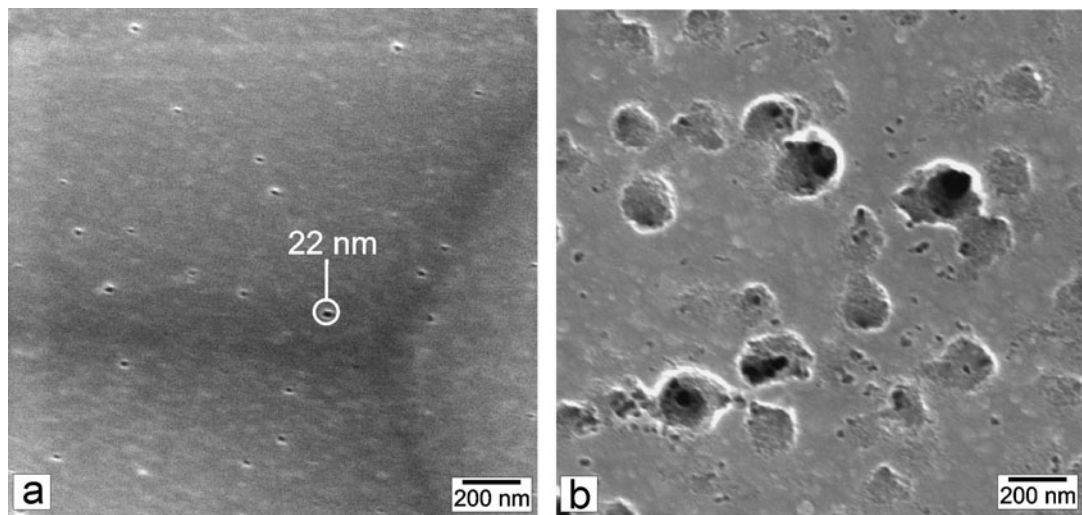


Figure 4. HRSEM images of surfaces of pyrolytic carbon coatings cooled down with 300 (a) and 6°C/h (b). The percentage fraction of surface pores is 0.2 (a) and 17% (b). The coatings have been deposited for 70 h at a temperature of 950°C and an ethene pressure of 4 kPa (Reznik et al, 2006).

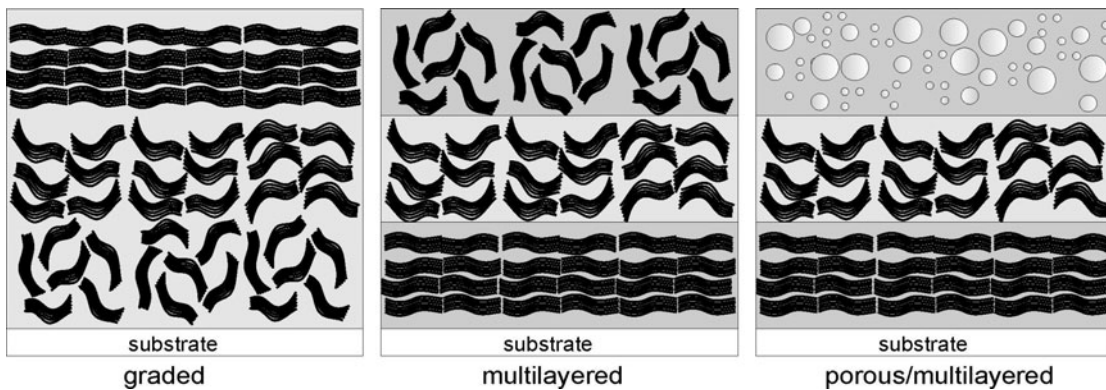


Figure 5. Concepts of coating systems