



Microstructural investigations of carbon foams derived from modified coal-tar pitch



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ABSTRACT

This work reports the microstructural evaluation of carbon foams derived from coal-tar pitch precursors treated with H₂SO₄ and HNO₃ and finally annealed at 1000 °C and 2000 °C. Our experimental investigations combine scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM) imaging, X-ray photoelectron spectroscopy (XPS) and micro-spot near-edge X-ray absorption fine structure (μ -NEXAFS) spectroscopy. This set of complementary techniques provides detailed structural and chemical information of the surface and the bulk of the carbon foams. The high-resolution microscopy data indicate the formation of carbonaceous amorphous microspheres (average diameters of $0.28 \pm 0.01 \mu\text{m}$) embedded in the partially graphitized carbon foam matrix at 1000 °C. The microspheres are enriched with sp-bonded species and their microstructural characteristics depend on the reagent (nitric vs. sulfuric acid) used for pitch treatment. A complete chemical transformation of the microspheres at temperatures >1000 °C occurs and at 2000 °C they are spectroscopically identical with the bulk material (sp²- and sp³-hybridised forms of carbon). The microstructure-property relationship is exemplified by the compressive strength measurements. These results allow a better description of coal-tar pitch-derived carbon foams at the atomic level, and may account for a better understanding of the processes during graphitization step.

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1. Introduction

During the last two decades carbon foam materials have received much attention due to their advantageous properties, such as low density, high mechanical strength, high thermal conductivity and low coefficient of thermal expansion (Inagaki et al., 2015; Gul and Yardim, 2015). Carbon foams are cellular structures that consist of randomly distributed pores with typical sizes between 100 and 500 μm . These unique properties, which mainly depend on the precursors' features and synthesis conditions, make carbon foams high performance engineering materials, and determine their many potential applications in numerous industries. Carbon foams can be produced as materials with thermal insulating properties, and could be applied as construction materials for airplanes, rockets and thermal management systems (Gallego and Klett, 2003; Klett et al., 2000). Carbon foams are promising radar absorbers, however these materials can be manufactured also with desired electrical resistance, dielectric constant and radar reflection coefficient,

suitable for advanced radar antenna construction (Fang et al., 2007; Yang et al., 2004). Carbon foams are relatively inert and stable even at high temperatures and radiation—they are suitable for nuclear shields and rods for nuclear reactors (Gallego et al., 2006). The inertness and mechanical strength of carbon foams determine the suitability of these materials for bone surgery materials, prosthetics and tooth implants (Mathieu et al., 2006).

Ford firstly prepared carbon foams by the pyrolysis of thermosetting polymer in 1964 (Ford, 1964). From there on, carbon foams were successfully produced by using coal, polyimide, melamine, resorcinol/formaldehyde, biomass materials like cork and olive stones, as well as from mesophase pitches as alternative precursors (Inagaki et al., 2015; Gul and Yardim, 2015; Kim et al., 2015; Nagel et al., 2014; Szeluga et al., 2015).

The effect of the precursor on the structure and properties of the obtained carbon foams is of great significance and it is under vast investigations (Klett et al., 2000). When coal-derived pitches are used as precursors, a preliminary treatment is usually required before the foaming process, in order to adjust the viscosity and plastic properties of the pitch that would allow an effective foaming process (Duk et al., 1986; Petrova et al., 2005). Recently, a relatively simple and low cost method was developed

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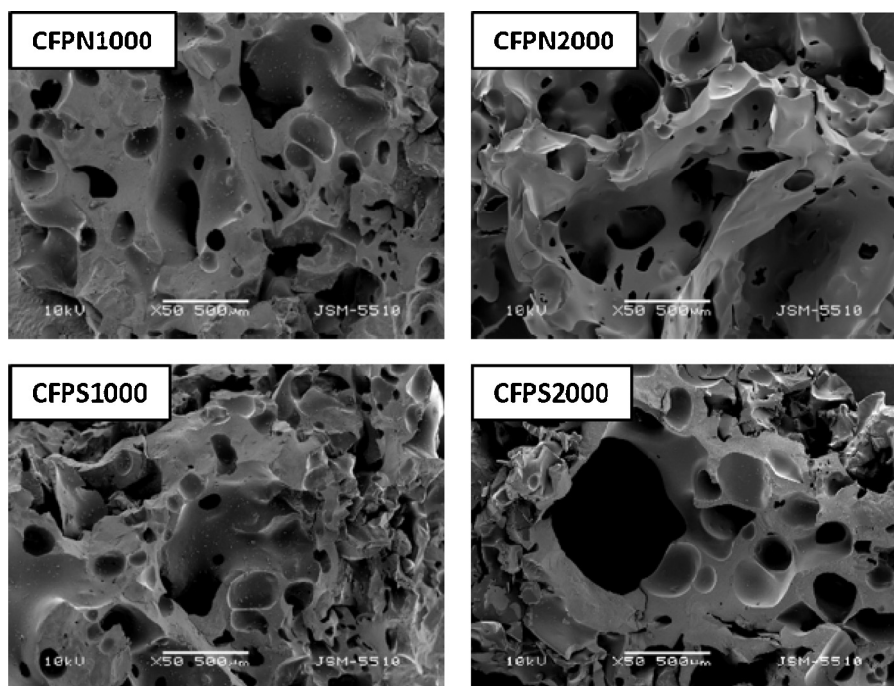


Fig. 1. SEM images of CFPN and CFPS foams.

for making mesophase-pitch-based carbon foams at low pressure and fast heating rate during the foaming process without a stabilization treatment (Tsyntsarski et al., 2010). Carbon foams with an anisotropic texture and high mechanical strength were produced using precursors obtained after thermo-oxidation treatment of commercial coal-tar pitch with mineral acids (Tsyntsarski et al., 2010). These carbon foams exhibit outstanding mechanical properties as well as a good performance as catalysts supports (Tsyntsarski et al., 2010; Velasco et al., 2010).

The microstructure of carbon foam materials is of key interest, since it determines their functional performances. Thus, a comprehensive characterization of the physical and chemical properties of carbon foams is required in order to obtain information on structure-property relationships. The goal of this work is to yield new insights into the micro- and nanoscale properties of carbon foams derived from commercial coal-tar pitch precursors treated with H_2SO_4 and HNO_3 and finally annealed at 1000°C and 2000°C . Herein, we report on the investigation of the latter carbon foams with emphasis on the correlation of morphological and electronic properties using scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and micro-spot near-edge X-ray absorption fine structure (μ -NEXAFS) spectroscopy. The obtained microstructural information is important for tailoring the properties of the coal-tar pitch precursor in order to achieve high performance carbon foam materials.

2. Materials and methods

The preparation of foaming precursors has been explained in details elsewhere (Tsyntsarski et al., 2010). In summary, the thermo-oxidation treatment of commercial coal-tar pitch with H_2SO_4 and HNO_3 was conducted at 120°C with continuous stirring. The modified samples were heated up to 350°C at atmospheric pressure and after that up to 580°C in a N_2 atmosphere, at pressure up to 1 MPa. The resultant “green” foams were calcinated at 1000°C in N_2 atmosphere to increase the strength and further evolving of volatiles. Finally, the resultant foams were heated consecutively

first at 1000°C for 1 h and then at 2000°C in Ar atmosphere. The carbon foams (CFPs) prepared from precursors treated with H_2SO_4 are denoted as CFPST, while the samples prepared from precursors treated with HNO_3 are denoted as CFPNT, where T indicates the final heating temperature (1000°C or 2000°C).

The morphology and the microstructure of the CFPs were analyzed by SEM (JEOL 5510) applying gold coating before the observation. The TEM investigations were performed on a JEOL 2100 scanning transmission electron microscope. The XPS studies were carried out on an ESCALAB MK II (VG Scientific) system with base pressure of 1.10^{-8} mbar. The XPS spectra were taken using an unmonochromatized Mg K α source ($h\nu = 1256.6$ eV) with the sample surface positioned normal to the detector. For carbon materials, this geometry provides XPS sampling depth of ~ 10 nm (McArthur et al., 2014). The C1s spectra have been fitted into spectral components using Lorentzian line shapes convoluted with a major Gaussian contribution as model functions.

Micro-spot near-edge X-ray absorption fine structure (μ -NEXAFS) spectroscopy and X-ray imaging were performed using the PolLux scanning transmission X-ray microscope (STXM) at the Swiss Light Source (SLS) (Raabe et al., 2008). For specimen preparation, CFP microparticles were deposited onto a Si_3N_4 window (Silson Ltd., Northampton, UK) of 100 nm thickness. The STXM chamber was turbo-pumped and the samples were imaged in transmission mode at about 5×10^{-6} mbar. The X-ray beam was focused with a Fresnel zone plate onto the sample and the transmitted photon flux was measured using a photomultiplier tube (Hamamatsu 647P) mounted behind the specimen, along the axis of the incident beam. Therefore, the technique is considered to be mostly bulk-sensitive. The diffraction limited spot size at the sample is determined by the width of the outermost zone of the zone plate, ~ 40 nm for the PolLux STXM experiments (Huthwelker et al., 2010). The PolLux STXM uses linearly polarized X-rays from a bending magnet in the photon energy range between 200 eV and 1200 eV. Carbon K-edge μ -NEXAFS spectra were collected in line mode, i.e., the transmitted signal was recorded while a line trajectory was scanned across the center of a particle at each value of the photon

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