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Carbon nanostructures on high-temperature ceramics – a novel composite material and its functionalization

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Abstract

A novel composite material consisting of a highly durable Si–B–N–C ceramic matrix modified by carbonaceous structures on the surface is presented. Depending on the content of Ni dopand of the starting polymer, a catalyzed growth of multiwalled carbon nanotubes (CNTs) of the bamboo-type or of carbon layers is observed. Due to the chemical resistance and thermal stability of both the ceramic support as well as of the carbonaceous surface layers, the material obtained has outstanding high-temperature properties and can be functionalized by metal particles deposited on the CNTs. Consequently, this material constitutes a unique backbone for catalysts.

Keywords: Ceramic; Bamboo carbon nanotube; Catalysis

1. Introduction

An intense research on carbon nanotubes (CNTs), their structure, and their physical and chemical properties was initiated by the pioneering work of Iijima in 1991 [1]. Although nanotubes have been found in various other systems since then [2], the CNTs are still outstanding and the most promising for applications since their superior chemical and physical properties are combined with an extraordinarily high stability and mechanical strength. In general, the research on carbon nanotubes and other carbonaceous materials is of great interest due to their high potential for applications in catalysis [3–5] as well as for surface modifications [6].

The classical approach to carbon nanotubes and carbonaceous materials is their synthesis via different types of catalyzed gas-phase decomposition of organic compounds by CVD, in autoclaves or arc reactors [7]. The formation of carbon micro-coils with various morphologies catalyzed by nickel has been reported, e.g. by Kuzuya et al. [8]. In general, morphology and structure of the carbon nanotubes obtained depends on several factors one of which is the catalytic species involved. Thus, a variety of different structural forms of carbon nanotubes have been described (see recent reviews, e.g. by Rao et al. [7] or by Ajayan [9]).

Especially, CNTs have been investigated as a heterogeneous backbone for carrying catalytic active metals. For example, CNT-supported ruthenium nanoparticles are highly active and stable catalysts in the ammonia system [10,11]. In another approach, mesoporous multi-walled CNTs loaded with nickel have been used for the selective oxidation of H_2S [12]. Finally, Rh-complexes have been grafted on oxidized CNTs for a selective hydrogenation of C–C multiple bonds [13].

In this work, we present new materials with a matrix of a highly durable Si–B–N–C ceramic, which is coated by different carbonaceous layers, and in particular with carbon nanotubes. The novel synthetic pathway described in the following section leads to a strong immobilization of the carbon material that is fixed on the ceramic support.

2. Experimental

2.1. Synthesis

All reactions have been carried out under argon atmosphere in dried reaction apparatus and solvents. A borazine-based polymeric silazane-precursor was synthesized as

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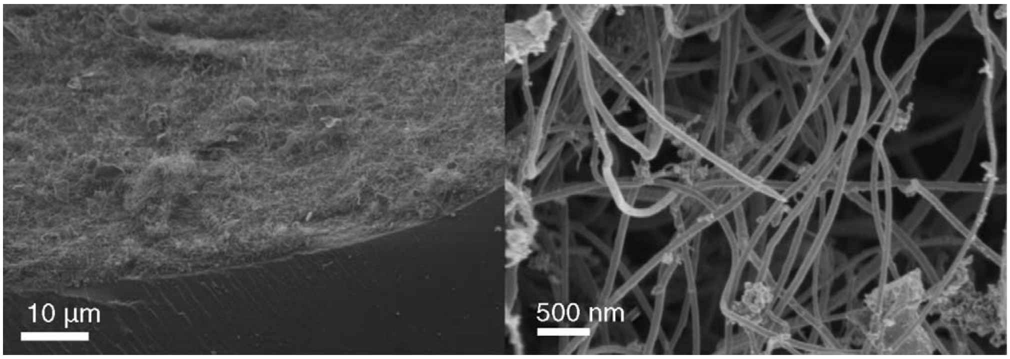

Fig. 1. SEM images of pure CNT-coated ceramic particles. Left: fractured piece. The CNT coating on top covers the amorphous Si–B–N–C ceramic matrix in the bottom area. Right: detail of the CNT coating (~80 nm in diameter).

described elsewhere [14]. Pyrolysis of the precursor to the ceramic was carried out in carbon crucibles (Sigradur) enclosed in a quartz tube. The metal particles were introduced using a wetness impregnation of the CNTs by the respective solution. Two times a droplet of the solution was added to the CNT coated surface. The wet solid was dried at room temperature and then heat treated in argon atmosphere at 500 °C for 12 h. The transition-metal compounds were purchased from ABCR ($Ni(C_8H_{12})_2$) and from Aldrich.

2.1.1. Ceramic/CNT support synthesis

(**A**) Approximately 500 mg of the polymeric precursor was diluted with 3 mL THF and a solution of 40 mg $Ni(C_8H_{12})_2$ in 5 mL THF was added. After stirring for 1 day under slightly reduced pressure, the solvent was evaporated completely and the viscous mixture was transferred into the carbon crucible. Typically, the pyrolysis was performed by a heating rate of 5 K/h to 800 °C, 20 K/h to 1000 °C, 5 h dwell and 10 K/h to room temperature. For (**B**), ~25 mg of the Ni-complex were used.

2.1.2. Metal solutions for impregnation

0.01 M $Ni(NO_3)_2$ in EtOH (**1**), 0.04 M $Fe(CO)_5$ in diethyl ether (**2**).

2.2. Characterization

IR spectra were measured on a Perkin-Elmer Spectrum 2000 NIR-FTRaman spectrometer (golden gate). Raman spectra have been recorded at a confocal Raman microscope (Labram, Jobin Yvon) at 632.8 nm wavelength (2 mW laser power). To evaluate the elemental ratios Si/Ni, the material was ablated by a 193 nm excimer laser (MicroLas, GeoLas) and, after atomization, a quadruple mass spectrometer (ELAN 6100 DRC ICP-MS, Perkin-Elmer) was applied for quantification.

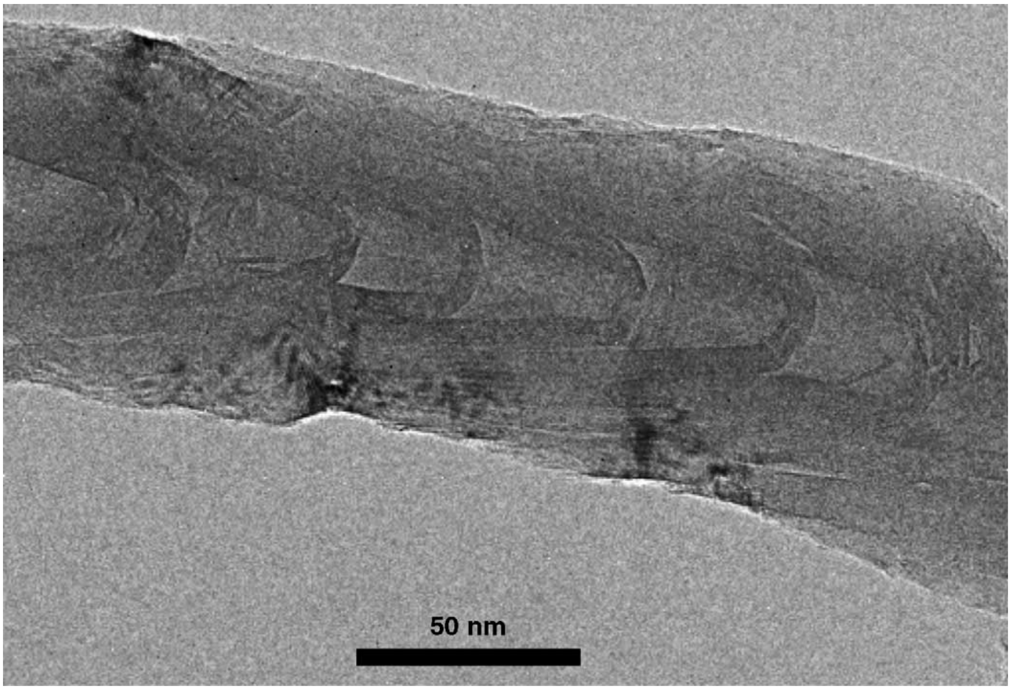

Fig. 2. Representative HRTEM image of the obtained bamboo-shaped multiwalled CNTs. Typically, the walls consists of 15–25 carbon layers.

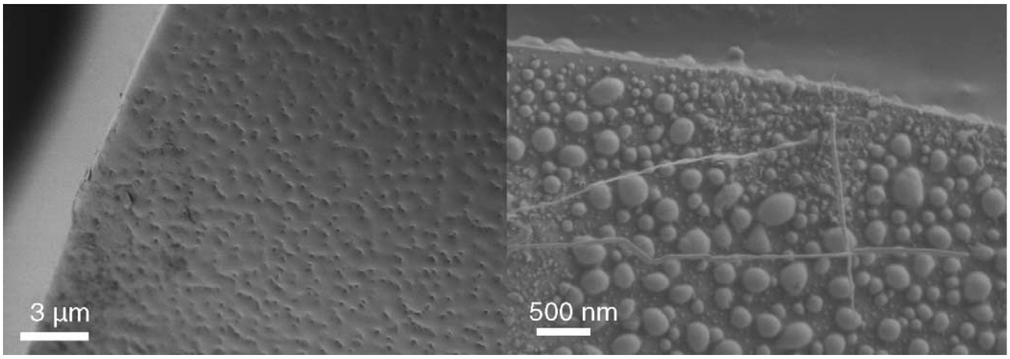

Fig. 3. Carbonaceous coatings of the ceramic particles. The layer structure depends on the Ni and carbon content of the precursor material.

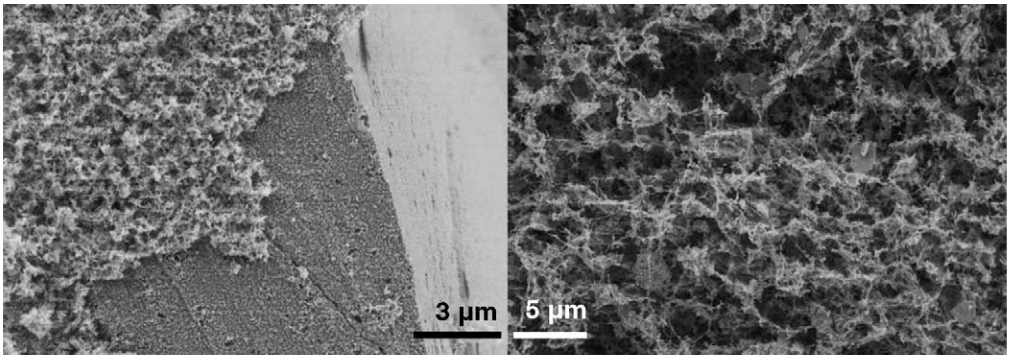

Fig. 4. Surface of the ceramic material from $Ni(NO_3)_2$/EtOH impregnation. An immobilized Ni/C layer can observed.

2.3. Electron microscopy

Scanning electron microscopy (SEM) images were recorded on a LEO 1530 (Zeiss, Oberkochen), operated at low voltage (V = 1 kV) to minimize charging of the as-synthesized samples. For (scanning) transmission electron microscopy (TEM, STEM), the CNTs were scratched directly from the ceramic pieces. After dispersing the material in ethanol, some drops were deposited onto a porous carbon foil supported on a copper grid. TEM studies were carried out on a CM30ST, STEM on a Tecnai 30 F (FEI, Eindhoven). The Tecnai 30 F is equipped with an EDAX detector for qualitative point analyses by energy-dispersive X-ray spectroscopy (EDXS).

3. Results and discussion

Recently, we reported on the precursor-directed formation of Si–B–N–C ceramics using substituted vinyl-borazine precursors [14,15]. These types of ceramics are thermally stable up to more than 1500 °C and show unique mechanical properties at high temperatures as well as a very low density (1.6–1.7 g/cm^3) [16]. Here, we present the synthesis of pure

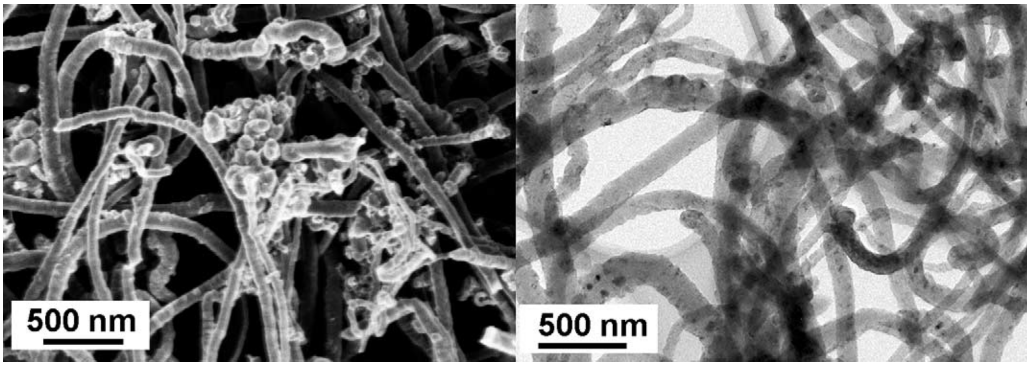

Fig. 5. CNTs on the surface of the ceramic particles after impregnation with $Fe(CO)_5$. Left: Bright dots on the CNTs represents metallic particles in the SEM image. Right: TEM image of the impregnated CNTs with metallic particles (dark dots).

multi-walled bamboo-shaped carbon nanotubes directly on the surface of the Si–B–N–C ceramic matrix [17]. The high-temperature ceramic material is completely coated by a fur-like surface of CNTs. Mixing the preceramic polymer with a solution of bis(1,5-cyclooctadiene)nickel results in a homogeneous distribution of the complex in the liquid polymer source. From IR spectroscopic investigations, two modes at 905 and 3070 cm^{-1} reveal the incorporation of the Ni-complex in the polymer without agglomeration or reaction, so far. Subsequent heating of the mixture under inert gas atmosphere causes the simultaneous pyrolysis of the polymer to form the ceramic matrix as well as the in situ growth of CNTs (**A**) or carbonaceous coatings (**B**), respectively. After a slow heat treatment of precursor **A** up to 1000 °C (see Section 2), a complete coating of the ceramics is observed that appears fur-like. Fig. 1 shows a view on the surface of the as-obtained material. The dense coating of the ceramics is evident in the SEM survey image (Fig. 1, left). A higher magnified image (Fig. 1, right) reveals that the coating consists of CNT in an almost pure form. Every carbon nanotube shows a coil-like behavior with different flank leads.

TEM investigations (Fig. 2) show the presence of multi-walled nanotubes with diameters mainly in the range 50–100 nm and wall-thicknesses varying widely. Remarkably, Ni particles have never been found at the CNTs. Inner cores of the CNTs exhibit a bamboo-like morphology formed by 5–15 carbon layers. The measured inter-layer distance of about 0.34 nm is similar to that in graphite and a typical value found in CNTs. Furthermore, the observed Raman modes (1327 cm^{-1} (D-band) and 1581 cm^{-1} (G-band)) correspond to that of carbon nanotubes and can assigned to the graphitic layers [18,19]. Up to now, no Y-junction was observed in this material.

The nickel metal incorporated in the preceramic polymer and the ceramics, respectively, must be considered as the catalytically active species for the formation of the carbonaceous materials. Since the samples are completely amorphous according to X-ray powder diffraction, the catalytic active Ni dots in the ceramic matrix are only a few nanometers in size. Especially the formation of coil-like CNTs and carbon rods is well known and in agreement with our observations [20]. Furthermore, a constant Si/Ni ratio has been measured all over the ceramic pieces by laser ablation ICP-MS [21,22]. Additionally, from depth profile measurements, a homogeneous spatial distribution of nickel in the matrix was also observed [23].

Using a lower Ni content in the preceramic precursor (**B**), a simple carbon coating of the particle surface can be observed (Fig. 3). The coarseness of the carbon surface layer can, to some extent be controlled by the amount of Ni and C in the precursor. A deeper investigation of the parameters for this surface layer formation is in progress.

Remarkably, it is possible to load the immobilized carbonaceous coating of the ceramic material with active metals for catalytic applications. First experiments to load the CNTs with metals have been successfully performed. For example, $Ni(NO_3)_2$ was added via wet impregnation onto the CNTs. As can be seen from Fig. 4, the CNTs are partially destroyed. Nevertheless, the left image in Fig. 4 shows that the ceramics is coated by an immobilized Ni/C layer.

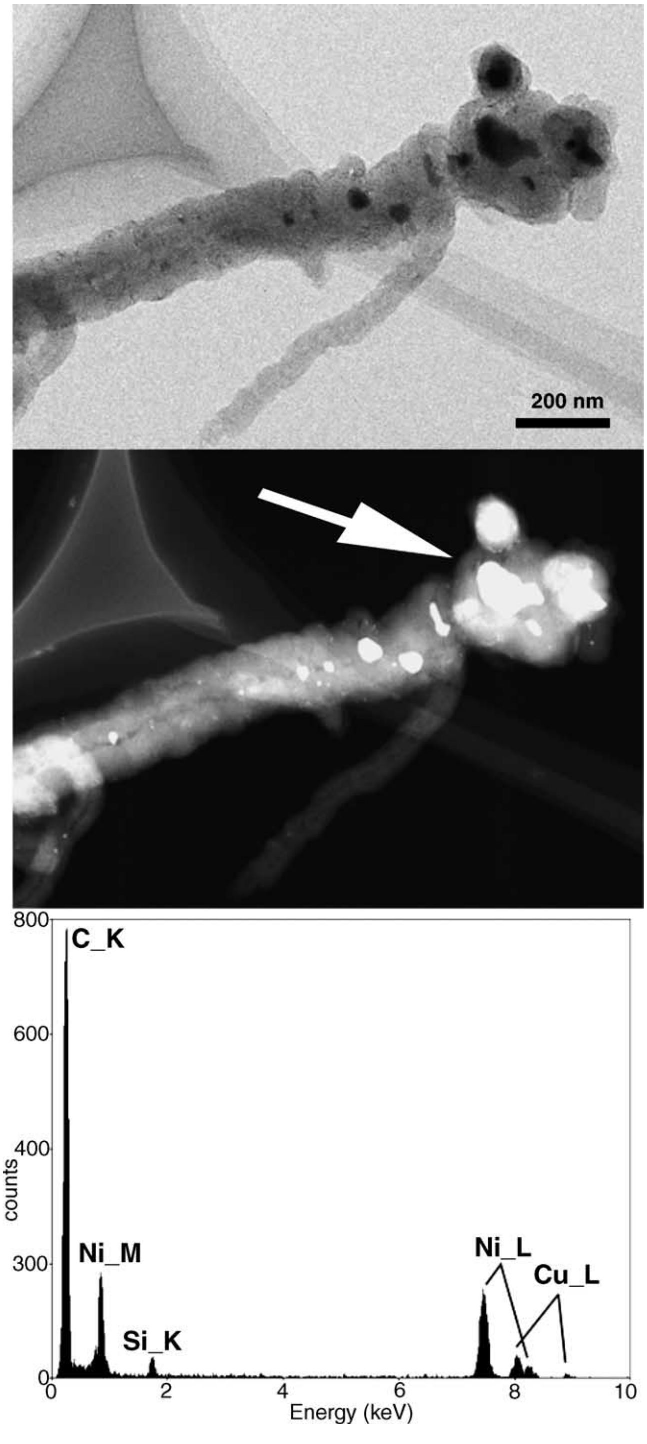

Fig. 6. Selected carbon nanotube after $Fe(CO)_5$-impregnation as well as Fe–Ni exchange (top: TEM image, middle: STEM image obtained with a high angle annular dark field detector). EDXS spot analysis (bottom) on the particle marked in the STEM image reveal the formation of Ni dots on the CNTs. The Cu signal is due to the copper grid which supports the carbon foil of the TEM specimen.

A similar experiment has been performed with $Fe(CO)_5$ (solution in ether). This metal source appears to be advantageous since it is easy to decompose at relatively low temperatures. After heating the sample at 500 °C, a partial impregnation of the CNTs as well as the formation of metal particles is observed (Fig. 5). Point analyses by EDXS reveal that the metal particles exclusively consist of Ni while no Fe was detected in several reproducible experiments confirming this result (Fig. 6). This is surprising since a transfer of the metal has taken part. Apparently, the iron formed in situ by decomposition of the carbonyl unhinged nickel from the ceramic matrix, which afterwards precipitated at the surface of the CNTs (Fig. 6). This metal exchange is probably caused by the much stronger affinity of Ni to the unsaturated carbon system of the CNTs compared to that of Fe [24].

4. Conclusions

The presented new composite material with a thermal stability up to 1500 °C of both the carbonaceous or nanotube coatings and the ceramic matrix opens a wide range for novel applications. Especially, a strong immobilization of the CNTs allows to use this material as a support for heterogeneous catalysts. The functionalization of the CNTs with metals via common impregnation methods is demonstrated exemplarily. By minimizing the ceramic particle size, large surface carbon nanotube materials might be achieved.

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