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Magnetic characterisation of pyrocarbon films obtained by chemical vapour deposition on alumina.

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Abstract

Pyrolytic carbon films deposited on alumina substrates by chemical vapour deposition starting from methane are analysed by measurement of static magnetic susceptibility, electron spin resonance and proton Overhauser shift. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chemical vapour deposition (CVD) in hot-wall reactors can be used to deposit various materials, if the flow of volatile precursors through the reactor can be realised. One typical example for this type of mechanism is the deposition of pyrolytic carbon (in the following abbreviated as pyrocarbon) on or in substrates starting from methane as the simplest form of a volatile hydrocarbon. It is well established that the interplay of homogeneous gas phase reactions, chemisorption and heterogeneous surface reactions is of considerable importance for CVD [1-3]. The relation of the free volume of the deposition space to the size of the surface area of the substrate is considered to be a decisive parameter. Especially due to their

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role for chemical vapour infiltration for carbonfiber-reinforced carbon, the understanding of the basic mechanisms is also of considerable technical relevance.

The current model for pyrocarbon CVD in hotwall reactors is based on two assumptions [1,2]:Homogeneous gas-phase reactions of methane lead to hydrocarbons with increasing number of carbon atoms and increasing carbon/hydrogen ratioThe rate of carbon deposition from various hydrocarbons or hydrocarbon radicals increases with increasing number of carbon atoms and carbon/hydrogen ratio.

It was shown earlier that hydrogen forms two kinds of carbon-hydrogen surface complexes, an "aliphatically bound" C– (H_2) and an "aromatically bound" C–(H) complex [2,3]. Whereas the first one is already decomposed at about 600°C, the latter one is rather stable with desorption becoming significant only above 1000°C (up to 1400°C). Evidently, the various magnetic resonance techniques could be

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rather useful for the distinction of different carbonhydrogen centres.

In this letter, we support the potentiality of magnetic measurements for the characterisation of the pyrocarbon preparation process via CVD in hot wall reactors. It was shown before that the combination of measurements of electronic transport, thermal and magnetic properties presents a specially reliable basis for the characterisation of different modifications of carbon [4]. In the current investigation, pyrocarbon is deposited (starting with methane) on alumina ceramic substrates and analysed with static and resonant magnetic methods as free-standing film after peeling off from the substrate.

2. Experimental details

The pyrocarbon samples were prepared by chemical vapour deposition on alumina ceramic substrates of 25 mm length, 20 mm width and 1 mm thickness. A tubular reactor was used consisting of an alumina ceramic reactor tube surrounding the conical inlet nozzle and outlet fitting made of pyrophillite and the central alumina ceramic tube forming the deposition space and supporting the alumina substrate [1,2]. For the sample preparation, an argon gas plug-flow with a partial pressure of 500 mbar of methane (total pressure 1013 mbar), a reaction temperature of 1100°C, a residence time of the vapour in the reactor of 0.32 s and a total deposition time of 6 h were adopted. Due to the difference in thermal expansion. the thick film at the rear end of the substrate cracked off during cool-down and could easily be peeled off. The magnetic properties could thus be characterised for such pyrocarbon films of several tens of microns thickness free of substrate. Due to the growth process, the pyrocarbon flakes were non-symmetrical and had glossy (lower) and frosted (upper) surface.

Static magnetic susceptibility was measured at 30 kG flux density with a Quantum Design MPMS SQUID magnetometer with the sample surrounded during measurements by a low-pressure helium atmosphere.

X-band electron spin resonance (ESR) spectra at 9.5 GHz were recorded with a Bruker ESP 300 E spectrometer equipped with an Oxford Instruments variable temperature gas-flow cryostat. The interac-

tion of the unpaired spins with the remaining protons in the pyrocarbon was characterised by Overhauser shift analysis [5].

3. Discussion of the experimental results

According to the current understanding [1,2], the pyrocarbon formed under the experimental conditions described above ought to approach a graphite-like carbon modification with delocalised (conduction) electrons, unknown concentration of localised (defect) spins (e.g. at dangling bonds) and a non-negligible concentration of remaining protons due to imperfect dehydration in the sequence methane — heavier hydrocarbon — pyrocarbon. Isolated protons may originate from CH groups at sp^2 as well as sp^3 carbon positions, proton pairs at CH₂ groups with a sp^3 carbon configuration. These entities can be distinguished by static and resonant magnetic measurements [6–8].

3.1. Static magnetic susceptibility

The variation of the static magnetic susceptibility of the non-oriented pyrocarbon sample with temperature measured in an external field of 30 kG flux density is shown in Fig. 1. The solid line fit with a temperature independent contribution and a Curie– Weiss law

$$\chi_{\varrho} = \chi_0 + C_{\varrho} / (T - \Theta) \tag{1}$$

gives $\chi_0 = 1.3 \times 10^{-6}$ emu/g, $C_g = 0.6 \times 10^{-4}$ emu K/g and $\Theta = -3$ K. Converted into approximate molar units (i.e. with $M_m \approx 12$ g/mol C, neglecting the hydrogen content), the Curie part of the magnetic susceptibility — $C_m \approx 7.4 \times 10^{-4}$ emu K/mol C — indicates a concentration of 1.9×10^{-3} unpaired electron spins S = 1/2 per carbon atom, a concentration that is not unusual for pyrocarbons [4].

In the lower part of Fig. 1, the quantity χT is plotted, that shows deviations from a pure Curie law more clearly. The small deviation from the straight line at low temperature and the small negative Curie–Weiss temperature $\Theta = -3$ K of the fit to Eq. (1) indicate weak antiferromagnetic interaction of the localised spins, at least for part of them. The antiferromagnetic interaction is not sufficient, however, to



Fig. 1. Static magnetic susceptibility χ of pyrocarbon films peeled off from alumina, shown as χ (on upper) and as χT versus temperature (on lower part). The experimental data (non-oriented films) were recorded at $B_0 = 30$ kG. The solid-line fit of Eq. (1) is explained in the text.

produce three-dimensional magnetic ordering in the temperature range of our measurements. Since according to the above estimate one unpaired localised (Curie-paramagnetic) spin resides only at every 500th carbon site, clustering of at least part of these spins seems a probable explanation for their non-negligible interaction. This was discussed in related systems earlier [7–9].

The fit parameter χ_0 or the positive slope in the χT plot of Fig. 1 do not allow a unique interpretation: $\chi_{0,m} \approx 16 \times 10^{-6}$ emu/mol C may be interpreted as the sum of temperature independent core diamagnetism (about -6×10^{-6} emu/mol C) and paramagnetism of delocalised electrons (Pauli paramagnetism). However, both observations may also reflect the contribution of magnetically saturated (i.e. ferri- or ferromagnetic) impurities like Fe or Fe₃O₄, because already the very small portion of 180 µg ferromagnetic iron per gram of the sample would be sufficient to explain the observed temperature independent magnetisation of 39×10^{-3} G cm³/g (at 30 kG). Therefore it is favourable that the temperature independent paramagnetic contribution of the delocalised electron spins with $g \approx 2$ can be observed independently and separately by ESR-intensity analysis.

3.2. Electron spin resonance

The ESR lines of the pyrocarbon films exhibit at 9.5 GHz a very small (motionally narrowed) width and approach Dysonian shape [10] as expected due to the electrical conductivity of the films (Fig. 2). The ESR-signal intensity is constant at temperatures above 100 K (Fig. 3), but increases with decreasing temperature below 100 K. In agreement with the static susceptibility analysis, anomalous behaviour is observed in the 5 K range. In the temperature range from 250 to 10 K, the peak-to-peak line-width decreases by about a factor of 3. This general behaviour is in agreement with earlier results for conductive polymers with localised magnetic impurities [9].

Generally, not all paramagnetic (localised) defects can be detected by ESR [9]. On the other hand, the $g \approx 2$ ESR-signal reflects the electron spin susceptibility residing at carbon-related centres or regions of the pyrocarbon sample especially clearly. If, therefore, the Curie-like part of the ESR-line intensity is identified with the Curie-like contribution of the static magnetic susceptibility (known in absolute units), an absolute value of $\chi_{P,g} = (1.0 \pm 0.2) \times 10^{-6}$ emu/g (or $\chi_{P,m} \approx (12 \pm 3) \times 10^{-6}$ emu/ mol C) for the high-temperature range (100–250 K)



Fig. 2. X-band ESR signal of pyrocarbon film recorded at T = 10 K, demonstrating weak distortion of the Dysonian ESR-line shape of the conductive sample.



Fig. 3. Variation with temperature of the peak-to-peak line width (upper part) and signal intensity (lower part) of the Dysonian shaped ESR line of the pyrocarbon sample. Note that a temperature dependence of the skin depth will influence the conversion from signal intensity into the *T*-dependence of the absolute spin susceptibility.

can be estimated, in close agreement with the value based on the static susceptibility.

3.3. Proton Overhauser shift

For the conditions of the sample preparation reported above, the hydrogen content of the solid pyrocarbon is expected to be non-negligible [1-3]. Indeed, isotropic hyperfine coupling of the electron spins to the proton nuclear spins is demonstrated by the Overhauser shift detected at X-band via ESR line shift induced by radio-frequency (RF) irradiation at the proton Larmor frequency of about 14.35 MHz. The distorted line shape of the observed shift ΔB_{OV} versus RF-frequency (Fig. 4) — a narrow line seems superimposed on the high-frequency part of a broader line — indicates the presence of at least two types of proton-carrying centres in the pyrocarbon sample. The latter is also indicated by the temporal evolution of the dynamic nuclear polarisation (DNP). As exemplified by the solid line fit in Fig. 5, the proton relaxation can be described at low temperature by a long and a short relaxation time, differing by more than a factor of ten.



Fig. 4. Overhauser shift of ESR line, recorded at T = 4.2 K for high microwave power $P_{\text{MW}} \approx 200$ mW. The distorted line shape of the proton Overhauser-shift signal is evident.

It is difficult to exclude that the description of the time dependence of the proton DNP with a distribution of relaxation times would also be appropriate, e.g. the fit by a stretched exponential function. This description was recently used for 13 C and 1 H NMR recovery in the hard form of amorphous hydrogenated carbon (a-C:H) [6–8]. It results there from localised paramagnetic centres aggregated in clusters. According to the static magnetic susceptibility analysis reported in Section 3.1, a non-uniform localised-spin distribution seems not unlikely to be realised for the pyrocarbon sample studied here. The main difference between both experimental condi-



Fig. 5. Temporal evolution of the proton dynamic nuclear polarisation (DNP) at T = 4.2 K after switch-off of the ESR saturation: The solid-line fit with two exponentials reveals the two different decay constants $T_{1,\text{short}} = 0.13$ s and $T_{1,\text{long}} = 1.56$ s.

tions should be taken into account, however. In the current investigation we deal with pyrocarbon samples of rather high electrical conductivity. Consequently, the proton-relaxation information has been recorded indirectly via ESR of the electron spins. Dynamic nuclear polarisation (DNP) and Overhauser shift measurement detect selectively those protons that interact with the electron spins via isotropic hyperfine interaction.

4. Concluding remarks

We have shown that the graphite-like pyrocarbon samples prepared by CVD from methane can readily be characterised by static and dynamic magnetic methods. In order to monitor the kinetics of CVD along the reactor axis by magnetic characterisation. sticking of the pyrocarbon film on the substrate is required. For this purpose, the deposition on highpurity boron nitride is preferable. The corresponding magnetic characterisation revealing e.g. the variation of the ESR line width by more than one order of magnitude along the substrate length of 25 mm is currently in progress. The measurement of the as-deposited films will also allow to characterise the anisotropy of these films that ought to be a by-product of development of the hexagonal graphite structure [11]. On the other hand, we have shown here that the deposition on alumina substrates offers the unique chance to obtain free-standing pyrocarbon films without peculiar efforts.

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