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Influence of reaction parameters on the attachment of a carbon nanofiber layer on Ni foils

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ABSTRACT

Dense carbon (C) and entangled carbon nanofiber (CNF) layers were deposited on nickel foils by decomposition of ethylene in presence of different H_2 concentrations at 450 °C for different reaction times. Both C and CNF layer thicknesses increase with time, but samples pre-oxidized at 500 °C normally lead to thinner CNF layers and thicker C layers, as compared to samples pre-oxidized and reduced at 700 °C. The mechanical stability of CNFs decreases with growth time, especially for oxidized-reduced samples. The addition of H_2 creates a maximum in the CNF thickness that coincides with a minimum in the C layer thickness, at 5% H_2 for samples oxidized at 500 °C and at 20% H_2 for samples oxidized-reduced at 700 °C. CNF layer stability increases with C layer thickness but decreases with CNF layer thickness. The ratio between the C layer thickness and the CNF thickness determines in the end the mechanical stability of the CNF layer.

1. Introduction

Carbon nanofibers (CNFs) [1–5] and carbon nanotubes (CNTs) [6–12] have recently attracted intense research efforts with the expectation that these materials have unique properties. CNFs and CNTs can be synthesized via three main processes: arc-discharge [13–16], laser ablation [17,18], or catalytic chemical vapor deposition (C-CVD). With regard to large-scale synthesis, the C-CVD route is by far the most feasible option in terms of cost and energy requirements. CNFs and CNTs offer various properties such as high surface area, high thermal and electronic conductivity, high mechanical stability and high inertness. These properties make CNFs and CNTs promising for many applications such as catalyst supports [19–22], batteries and fuel cells [23–25], hydrogen storage [26,27], polymer reinforcements [28,29], super-capacitors [30], sensors and nanoprobes [31] and super-hydrophobic layers [32,33]. CNFs offer advantages over CNTs such as a lower growth temperature and higher amount of surface defects acting as anchoring sites [6,8]. Our main interest is in applications of thin layers of CNFs supported on structured materials, i.e. foams, foils and other surfaces.

In general, the growth of carbon nanostructures requires catalyst nanoparticles (usually Ni, Fe, or Co), a carbon feedstock (hydrocarbon or CO) and high temperatures (400–1000 °C). The most commonly accepted mechanism for the growth of CNFs was postulated by Baker et al. on pre-shaped Ni nanoparticles [34]. According to this mechanism, the hydrocarbon first decomposes on the surface of a metal nanoparticle, then carbon diffuses through the particle and finally, it precipitates to form the carbon filament. However, earlier study in our group [35] showed that CNFs and a dense carbon layer (C layer) grow simultaneously on Ni foams, suggesting that an alternative mechanism might occur on polycrystalline materials. This C layer looks apparently dense but it has high surface area [35]. The C layer forms between the substrate and the CNF layer and facilitates the attachment of the C and CNF layers to the substrate. The deposition of a dense C layer and carbon filaments on metal foils has also been reported in literature [36–41].

One advantage of growing CNFs on polycrystalline metal, e.g. foils, is that deposition of catalyst nanoparticles is not needed. Apparently, nanoparticles are created either as a result of any pretreatment or during the initial stages of carbon deposition [41,42]. However, the type of pretreatment determines the carbon deposition rate [42,43]. Moreover, it is well known that addition of H_2 during catalytic CNF growth influences both the carbon deposition rate as well as the morphology of the CNFs. Hydrogen is known to either accelerate [44–51] or suppress [52–54] the formation of CNFs or CNTs depending on the H_2/hydrocarbon ratio and the type of catalyst. High H_2 concentrations normally lead to low initial deposition rates, but the total level of deposition increases because of reduced deactivation rates. The addition of H_2 has also been reported to decrease the diameter of CNFs [55–58].

Formation of carbon and CNFs on metal surfaces has been studied extensively in the past because these phenomena are a nuisance in e.g. stainless-steel reactor pipes in steam-cracking units, operating at temperatures higher than 700 °C [59,60]. In contrast, controlled preparation of CNF layers on pure metals, aiming at preparation of a functional material, has not been studied in great detail so far. Furthermore, characterization of CNF layers on flat surfaces in terms of

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mechanical stability has not been sufficiently addressed [61,62]. Mechanical stability is of crucial importance when aiming at applications of the resulting materials as catalyst support [19,58], nanoelectronics [63,64], polymer reinforcement [65] or super-capacitors [66,67]. Poor mechanical stability would not only compromise the performance for the targeted applications, but loose fibers could also induce a risk for human health [68,69]. There are no systematic studies available on the influence of reaction conditions on the attachment of dense and filamentary carbon layers on Ni foils.

In our previous work [43], we observed that homogeneity and attachment of carbon layers deposited on different metal foils at 600 °C varied with the composition of the metal foil, addition of H_2 and type of pretreatment. We also reported [35,70] that polycrystalline Ni surface induces the formation of CNFs rather than CNTs at ca. 450 °C. In the present work, we report on the factors that control the attachment of the CNFs to a Ni foil. We have systematically studied the influence of reaction parameters, such as H_2 concentration, reaction time and pretreatment, on the attachment of the C layer and CNF layer on nickel foil.

2. Experimental

2.1. Materials

Nickel foils (0.1 mm thick, 99.5%, Alfa Aesar) were used as active catalytic substrates. Square sample pieces (10 × 10 mm) were prepared from the as-received sheet by wire cut electrical discharge machining (Agiecut Challenge 2). The foils were degreased ultrasonically in acetone and dried at room temperature before being loaded into a quartz tube. Hydrogen, nitrogen and air (99.999%, Praxair), and ethylene (99.95%, Praxair) were used for CNFs formation without further purification.

2.2. Carbon nanostructures formation

An in-house built vertical catalytic chemical vapor deposition (C-CVD) reactor was used to grow carbon nanostructures. It consists of a 12 mm inner diameter quartz reactor. The temperature was raised in N_2 from room temperature to the desired temperature at a rate of 7.5 °C/min. The samples were first pretreated according to two different methods. The first pretreatment consists of oxidation in air (20% air and balance N_2) under a total flow rate of 100 cm^3/min for 1 h at 500 °C. The second pretreatment consists of oxidation in static air for 1 h at 700 °C followed by reduction in hydrogen (20% H_2 and balance N_2) for 2 h at 700 °C. N_2 was used to flush the reactor for 5 min, for safety reasons, when switching between air and hydrogen. The different pretreatments will be denoted as Oxid 500 and Oxid/Red 700 respectively.

After the pretreatment, the temperature was adjusted to 450 °C in N_2. The CNFs were grown using a gas mixture of hydrogen and ethylene (C_2H_4) in nitrogen with a total flow rate of 100 cm^3/min. The concentration of C_2H_4 (25% v/v) was kept constant in all experiments and the nitrogen flow was adjusted whenever hydrogen concentration (0–50%) was modified. The CNF growth time was varied between 5 and 180 min. Finally, ethylene and hydrogen (if used) gas streams were shut off and the system was cooled down to room temperature under 100 cm^3/min of N_2 at a rate of 10 °C/min.

2.3. Characterization

The mechanical stability of the carbon layers was characterized by flowing nitrogen (120 dm^3/min) for 1 min over the flat samples in a cylindrical quartz tube (11 mm in diameter) at a linear speed of 21 m/s. The attachment of the carbon layers was assessed by the difference in weight between the sample after synthesis, including loose carbon, and after blowing it with nitrogen. The weight loss percentage is calculated accounting for the total weight of carbon deposited. The weights were calculated using a Metler Toledo AE163 balance with precision up to 0.01 mg. The morphology and cross sections of the carbon layers were studied using a scanning electron microscope (SEM) JEOL 6250LV, equipped with secondary electrons detector. Cross sections were obtained by cutting the samples with scissors after immersing them shortly in liquid N_2 to prevent the loss of the weakly attached fibers. The averaged thicknesses of the carbon layers were calculated from 10 measurements of the thickness at different locations at cross section in SEM pictures using the freeware ImageJ [71].

3. Results

Fig. 1 shows one typical top view morphological picture of a dense C layer (Fig. 1a), a porous and entangled CNF layer (Fig. 1b) and one cross section picture clearly showing a dense C layer under a porous CNF layer (Fig. 1c), typical for the results obtained in this study. In contrast to our previous work on CNF growth on Ni foils at 600 °C [43], all the samples of the present study at 450 °C present either homogenous dense carbon layers or homogenous CNF layers.

3.1. Influence of pretreatment

Fig. 2 shows the morphology of the fresh and pretreated Ni foil. The fresh sample (Fig. 2a) does not show clear grain boundaries. However, oxidation at 500 °C (Fig. 2b) induces the formation of grains in the range of 5–20 μm. The typical weight increase after oxidation at 500 °C is 0.08 mg, resulting in an estimated thickness of 60 nm of NiO (density 6.7 g/cm^3 [72]). Oxidation–reduction at 700 °C (Fig. 2c) creates grains in the range of 0.5–5 μm, in agreement with our previous

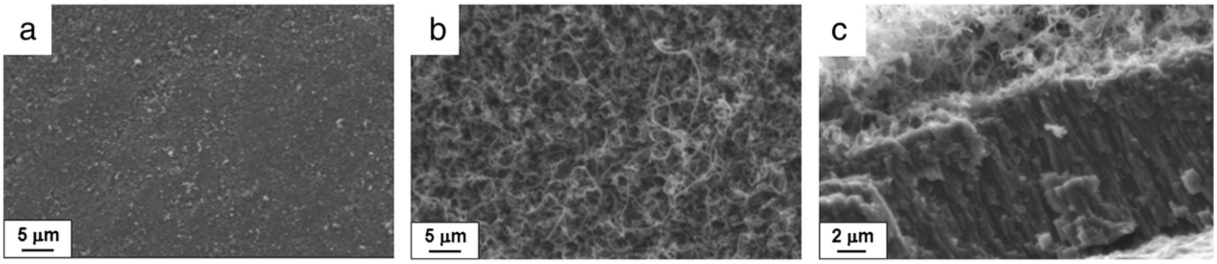

Fig. 1. Representative SEM pictures of carbon layers obtained at 450 °C before the air flow test. a) Dense C layer grown on an oxidized/reduced sample after 60 min of reaction and 0% H_2; b) porous and entangled CNF layer grown on an oxidized/reduced sample after 60 min of reaction and 10% H_2; c) cross section showing both C and CNF layers grown on an oxidized sample after 60 min and 0.3% H_2.