Chemical Physics Letters 685 (2017) 259–262

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

One-step synthesis of nitrogen-doped carbon nanofibers from melamine over nickel alloy in a closed system

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ARTICLE INFO

Article history:
Received 28 June 2017
In final form 27 July 2017
Available online 28 July 2017

Keywords:
Nitrogen-doped carbon nanofibers
Closed reaction system
Self-organized catalyst
Nichrome
Ferromagnetic resonance

ABSTRACT

A novel approach to the synthesis of nitrogen-doped carbon nanofibers in a closed system at elevated pressure with the use of bulk Ni-Cr alloy as a catalyst precursor was proposed. Melamine was chosen as a substrate containing both carbon and nitrogen. Method of ferromagnetic resonance was applied for diagnostics of dispersed Ni particles appearance. The process of corrosion of a bulk alloy followed by formation of dispersed Ni particles catalyzing the growth of nitrogen-doped carbon nanofibers was found to take place at temperatures above 560 °C. The final content of nitrogen in obtained carbon nanofibers was about 10 at.%.

1. Introduction

As well known, carbon nanofibers (CNF) are considered as materials having wide perspectives to be applied in different areas of science and technology. Thus, they seem to be efficient in production of composites based on industrially derived polymers, electrodes for lithium-ion chemical current sources, electrodes for supercapacitors and fuel cells, etc. [1–4]. Besides that, this class of materials is characterized with high mechanical strength, chemical purity and inertness that make it attractive to be used as a catalyst support [5–8]. In order to improve some properties of CNF (for example, adhesion, reactivity, electric conductivity), introduction of heteroatoms into the structure of carbon nanofiber is usually implemented. Thus, due to enhanced electrical conductivity and corrosion resistance, nitrogen-doped carbon nanofibers (N-CNF) attract a great attention for such electrochemical applications as catalytic oxygen reduction, lithium-ion storage systems, and others [9–12].

Conventionally, CNF are produced via catalytic chemical vapor deposition (CCVD) of different hydrocarbons (methane, ethane, ethylene, acetylene, etc.) over metals of iron subgroup (Fe, Co, Ni) and their alloys [13–20]. The catalysts, as usual, also contain a support or textural promoter, which is aimed to stabilize the metal particles in disperse state. The synthesis of CNF is performed in a flow regime, while the doping with nitrogen is achieved by addition of nitrogen precursor (ammonia, pyridine, melamine, methylimidazoles, etc.) into the reaction mixture [21–24].

In present work, a new approach for the synthesis of N-CNF is proposed. First of all, one organic substrate (melamine) was used as a source of both carbon and nitrogen. Secondly, the catalyst consisting of dispersed Ni particles was self-organized under reaction conditions from bulk nichrome precursor as a result of disintegration process. This process is well known in the literature as 'metal dusting' or 'carbon erosion' [25,26]. And finally, the synthesis was carried out in a closed reactor system under elevated pressure. Thereby, overall process including catalyst preparation, CNF synthesis and doping with nitrogen is being realized in one step. Melamine used in present work as a substrate is affordable solid compound containing 40 at.% of nitrogen. Commercial nichrome wire was used as a bulk catalyst precursor. Initial stages of its disintegration were studied by means of ferromagnetic resonance technique [27,28].

2. Experimental

The experiments were performed using the quartz ampoules (d = 4–5 mm, V ~ 0.2 ml) as a reactor. A piece of nichrome wire of about 0.2–0.3 mg was placed inside the ampoule together with 2–3 mg of melamine. Then, the ampoule was sealed and brought to thermal treatment at certain temperature for 2 h. The accuracy of temperature measurements was ±2 °C.

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http://dx.doi.org/10.1016/j.cplett.2017.07.073
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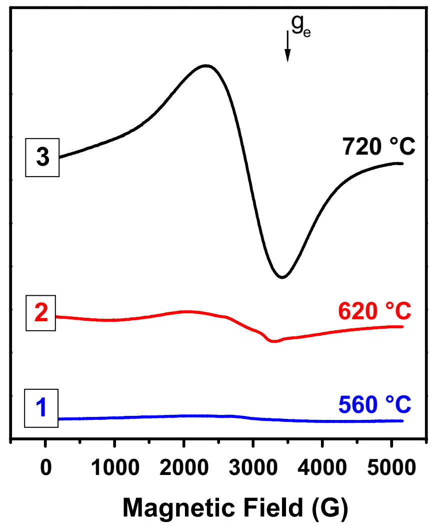

Fig. 1. Effect of the reaction temperature on FMR spectra for the bulk Ni-Cr alloy (nichrome) exposed to melamine in a closed reactor system.

The FMR spectra of the samples in sealed ampoules were registered at room temperature using an experimental setup based on an ERS-221 ESR spectrometer described elsewhere [29]. The processing of the spectra obtained was performed with the use of ESR_CAD software developed earlier.

After the measurements, the ampoules were carefully opened for further microscopic studies. The obtained N- CNF were studied by scanning electron microscopy (SEM) on a JSM-6460 (Jeol, Japan) electron microscope with a resolution of 4 nm in the range of magnifications from 5 × to 300 000 × . The local energy-dispersion X-ray (EDX) microanalysis was carried out using EDAX spectrometer with energy resolution 127 eV. Unfortunately, the amount of solid-state product was insufficiently small to study it with a wide range of characterization techniques.

3. Results and discussion

As it was recently reported [26,30–34], metal dusting of bulk items, which is mostly considered as an important and complicated problem in chemical industry [25], can be effectively applied for a synthesis of self-organized catalysts for CNF production. Such catalysts being formed under aggressive carbon-containing atmosphere are represented by dispersed metal particles with uniform composition and size. They showed excellent catalytic performance towards decomposition of a variety of hydrocarbons giving the superior values of CNF yield if compare with other especially prepared catalytic systems. Both the temperature and the nature of organic substrate were found to play a defining role for the metal dusting process. It should be noted that the process is characterized with existence of prolonged induction period, when the structural changes of the bulk metal surface and primal formation of dispersed particles take place. The duration of induction period strongly depends on the temperature. As usual, after the induction period, the metal item undergoes fast disintegration with formation of bunches of CNF. Detailed studies on the induction period and overall metal dusting process in 1,2-dichloroethane atmosphere by a set of physicochemical methods have revealed that FMR method is the most applicable to follow the very beginning period of metal dusting process [27,28]. Thus, in the case of nichrome wire, an appearance of FMR signal evidently indicates the formation of primal dispersed nickel particles. Unfortunately, the application of this approach is limited by the large amount of formed CNF due to significant microwave adsorption.

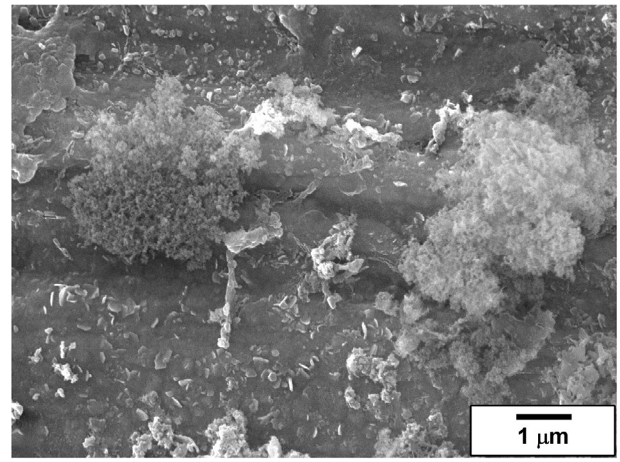

Fig. 3. SEM image of nichrome wire interacted with melamine at 620 °C.

Fig. 1 shows the evolution of FMR spectra in the course of melamine interaction with nichrome wire inside the sealed ampule (closed reactor system) at different temperatures. It should be noted that nichrome wire, as opposed to nickel, does not exhibit ferromagnetism at room temperature, and thus does not give a FMR signal [27]. It allows us to study the very beginning stages of the disintegration process by appearance of corresponding FMR spectra. No disintegration process followed by self-organization of ferromagnetic dispersed Ni particles was observed at temperatures of 500 °C and below. Weak FMR signal characterized by wide single band with typical for Ni parameters $g \sim 2.3$ and ΔH = 500–1100 G has appeared only at 560 °C, thus indicating the beginning of the disintegration process of the bulk alloy.

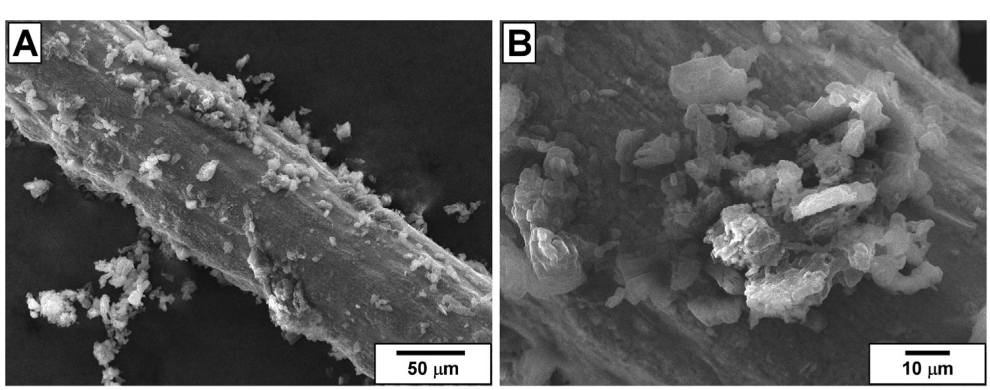

Fig. 2. SEM image of nichrome wire interacted with melamine at 560 °C.