

Nucleation and growth of carbon nanoforms on the surface of metallic plate-substrates and the mechanism of their doping with the clusters of ferromagnetic atoms

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Abstract

The present work deals with the special experiments on SEM-EDX study of morphology, chemical composition and topological transformations of the initial ground surface of the bulk iron plate-substrate after its interaction with the ethanol vapor pyrolysis products at high temperatures in the closed-loop and open cycle reactors. Our experiments have shown that the mechanism of formation of Fe clusters-doped CNFs on plate-substrate surfaces may be represented as a process, the first stage of which is a protonation of the substrate subsurface layers caused by diffusion of hydrogen atoms facilitating the formation of 3D nano-groups of Fe atoms assembled in the characteristic clusters with magic numbers of atoms, depending on the thermodynamics of the metal. The spontaneous coalescence of these clusters into giant Fe-clusters at comparatively low temperatures and formation of iron nano-droplets at comparatively high temperatures results in the formation of a nanopatterned surface with the uniformly distributed catalytic centers of CNFs nucleation. The second stage of the process is a nanoparticle-guided growth through the VLS or VS (at low temperatures) growth mechanisms in which the one cluster provides a nucleation of only one CNF particle so that the sizes of the nucleation centers determine the basic size of the CNF nanoparticles. Copyright © 2018 VBRI Press.

Keywords: Doped CNFs, clusters, growth mechanism, metal plate-substrate, SEM-EDX.

Introduction

The possibility of obtaining magnetic carbon nanopowders doped with the clusters of ferromagnetic (Fe, Co) atoms was first demonstrated in the authors' previous work [1, 2], using a novel technology combining the ethanol vapor pyrolysis and the CVD. The syntheses of the magnetic carbon nanopowders were performed on the ground flat surfaces of the metallic (Fe, Co) bulk plate-substrates (not powders), located in a horizontal continuous closed-loop reactor, operating in the mode of recirculation of the products of ethanol pyrolysis at 1200°C. The scanning electron microscopic (SEM), energy dispersive x-ray spectroscopic (EDX), and Auger electron spectroscopic (AES) analyses of the obtained magnetic carbon nanopowders, synthesized in different temperature zones of the reactor, were performed. It was shown that, depending on the synthesis parameters, the nanopowders mainly consist of either individual nanocompositional core-shell-type spherical carbon nanoparticles (CNPs with the diameter 150 ÷ 250nm in the form of carbon/graphene shells with the cores composed of Fe/Co atomic clusters) or of individual

carbon nanotubes (CNTs with the diameter ≤ 200 nm and the length of ~1 μm in which the atomic cluster is mainly located at one end of the nanotube, exactly in the inlet of the CNT channel [3, 4]), or of carbon nanobelts (CNBs) of almost uniform width ~300 ÷ 2000 nm and thickness ~ 60 ÷ 100 nm [5]. Here should be noted that the proposed technology of the synthesis of the core-shell-type CNF particles doped with the ferromagnetic atomic clusters is distinct from the conventional production processes of the same products because of its ability to perform a one-step simple doping process in a single cycle [2].

The interest in CNF nanoparticles has been permanently growing in the last decade in connection with the development of nanotechnologies for controlling the size and shape of nanoparticles as well as creating the ways for modifying their magnetic, optic, electronic and mechanical properties by doping them with different atoms and/or clusters. A particular interest is associated with the fabrication of core-shell-structured nanocomposites on the basis of the CNFs (CNT, CNP, CNB, CNW) doped with the ferromagnetic atom clusters for the synthesis of nanostructured functional materials which generate

properties that are not available in any other material [6-8]. Such materials give us a unique opportunity to better understand the fundamental concepts of the role of dimensionality and the size in their physical, chemical and functional properties. They have emerged as a new class of advanced materials with a tremendous potential of their diversified applications, mainly in the fields of advanced energy systems, gases (CO₂, H₂, etc.) capturing/storage systems and the syntheses of new hybrid functional polymer-based nanocomposite materials [7-9]. Clearly, to achieve further developments in this field it is necessary to elaborate a more fine-tuned controlling process of the synthesis of monodisperse nanopowders composed of core-shell-type CNF particles doped with atomic clusters of the required size and shape, which will be directly adaptable to the sintering of different new functional nanocomposite materials.

The solution to this important scientific and technological problem needs an enhanced understanding of the mechanisms of formation of CNFs doped with the metallic atom clusters. Thus, the aim of the work was to answer the questions: how the clusters of metallic atoms as the building blocks for the core-shell-type nano-scale-structure CNF particles behave at the interfaces, and whether they can be patterned or assembled into the observed free-poured state CNPs, and CNTs, and what is the determining factor of their base sizes at the commencement of growth? With this purpose, special experiments were performed for subsequent SEM-EDX study of morphology, chemical composition and topological transformations of the initial ground surface of the bulk iron plate-substrate after its interaction with the ethanol vapor pyrolysis products at high temperatures.

Experimental

Special experiments were performed in the present work to study the exact structural mechanism of direct synthesis of a core-shell-type ferromagnetic atom clusters-doped CNFs on the surface of a bulk iron plate-substrate, without the preliminary deposited catalyst materials (nanopowders or film catalyst precursors). Rectangular and disc-shaped cylindrical substrates with fine-grounded surfaces and the dimensions 40x15x3 mm and Ø20x5 mm respectively, suitable for the experiments and the SEM analytical chamber, were machined from the commercial polycrystalline Armco iron.

The syntheses of magnetic carbon nanopowders, composed of Fe atom clusters-doped single CNTs (or CNPs) were realized on the surfaces of the above substrates which were located in the 1200°C and 650°C temperature zones of the horizontal reactor of the experimental set-up described in [1, 2]. The syntheses were performed in two different regimes: first, in the mode of recirculation of ethanol vapor pyrolysis products in a closed-loop cycle reactor under the controlled partial pressure of oxygen in the range

10⁻²⁵ ÷ 700 torr, and the second, in the mode of flow of basic reagents (pyrolysis products of ethanol) in the open cycle reactor. In both cases, the ethanol pyrolysis was conducted at 1200°C, and the substrates were exposed in the above temperature zones for 30 min and 6h respectively. Next step of preparation of the substrate samples for SEM-EDX study included removing of the synthesized carbon nanopowder from a part of the substrate surface via shaking. Subsequently, a piece of the free poured nanopowder was attached to the SEM sample stage using a conductive adhesive.

The morphology, chemical composition and topological transformations of the ground surface of the bulk iron plate-substrate after its interaction with the ethanol vapor pyrolysis products at high temperatures and the distribution of CNF particles of the synthesized magnetic carbon nanopowders were examined using the scanning electron microscope JSM-6510LV (JEOL, Japan) with EDX spectrometer.

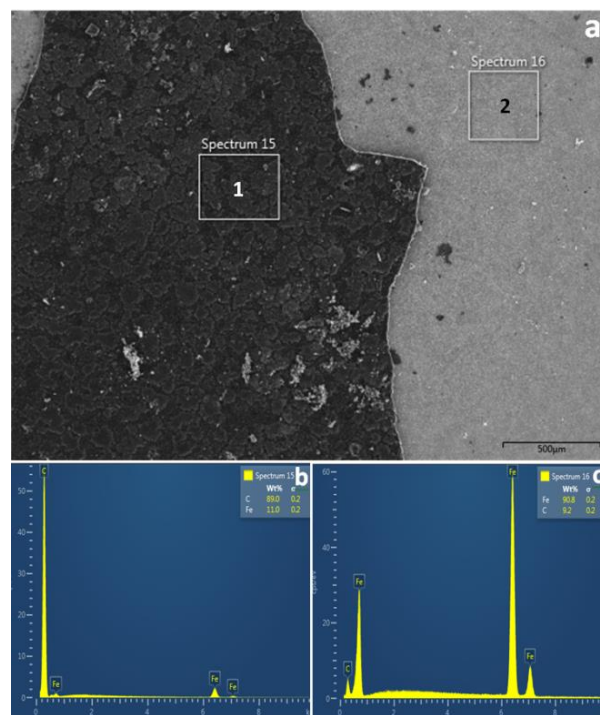


Fig. 1. SEM image of the Armco iron substrate surface after its exposure at 1200°C for 6 h in the closed-loop reactor in the mode of recirculation of the ethanol vapor pyrolysis gaseous products (a), EDX spectrum taken from the surface of the product synthesized on the substrate (area 1) (b), and the EDX spectrum taken from the substrate surface free of the synthesized product (area 2) (c).

Results and discussion

The representative SEM image of the Armco iron substrate surface after its exposure at 1200°C for 6 h in the closed-loop reactor in the mode of recirculation of the ethanol vapor pyrolysis gaseous products (C, CO, H, H₂, O, O₂) is shown in **Fig. 1.a**. Here, two neighboring areas are revealed on the surface: area 1 - the surface with the stratum of the synthesis' product, ~30 μm in width, and the area 2 - the

substrate's free surface after removing the synthesized product via shaking. The EDX spectrum taken from the substrate surface free of the synthesized product (**Fig. 1.c**) shows the following composition, ~ 90wt% Fe and ~ 10 wt % C. The more detailed analyses of the noted areas, using the magnified SEM images and the local EDX spectra obtained from different sites of the same areas, revealed the characteristic morphological and compositional peculiarities of transformations of the synthesized products and the substrate surface.

Fig. 2.a-d show the enlarged SEM images of the characteristic morphology and the corresponding EDX spectra of the free-poured nanopowder (**a, b**) removed from the area 2, and the substrate surface area (**c, d**) marked in **Fig.1.a**. It is obvious that the product synthesized in the above-described mode consists of individual nanocompositional core-shell-type CNTs ($\varnothing \leq 250$ nm, and the length up to $10\mu\text{m}$) in which the Fe atomic cluster incorporated in carbon shell is mainly located at one end of the nanotube, exactly in the inlet of the CNT's channel (**Fig. 2.a**). The average composition of the free-poured carbon nanopowder composed of the above magnetic nanoparticles was determined by EDX, and was equal to wt% Fe : wt% C $\approx 1 : 10$ (**Fig.2.b**). The values are in a good coincidence with the qualitative calculations based on the experimentally determined geometry and dimensions of the individual doped CNTs and the Fe atomic clusters incorporated in them. It is evident that variation of the synthesis parameters (temperature gradient between the substrate and the pyrolysis' gaseous product, speed of gaseous phase flow, partial pressures of the reagent gas components), makes it possible to reduce the length of the doped CNT to even zero, and thus form the spheroidal core-shell-type carbon nanoparticles doped with the Fe atom clusters [3, 4]. Consequently, it is possible to vary the percentage of the components in the synthesized magnetic carbon nanopowders within a certain range.

A valuable information, contained in the SEM image of the Armco-iron substrate surface (**Fig.2.c**) with the characteristic morphology formed in the process of interaction with the gaseous reagents of ethanol pyrolysis' products exposed at $1200^{\circ}\text{C} - 6\text{h}$, was revealed after removal of the synthesis' product from the substrate's surface. It is evident that because of the considerable structural and morphological transformations taking place in the surface layer of the ground iron plate-substrate, a nanopatterned surface with the practically uniform distribution of the spheroidal droplets was formed (**Fig. 2. c**).

Moreover, the EDX spectra obtained from each of the droplets show that they represent solidified iron atomic clusters of practically the same composition, covered with carbon nanoshells (**Fig. 2.d**). Here should be noted that the observed high contrast in the SEM images of the droplets' is caused by a simultaneous occurrence of the reflected initial electron beam (20keV) and the transmitted secondary electrons in the image forming detector, which in turn is supported by

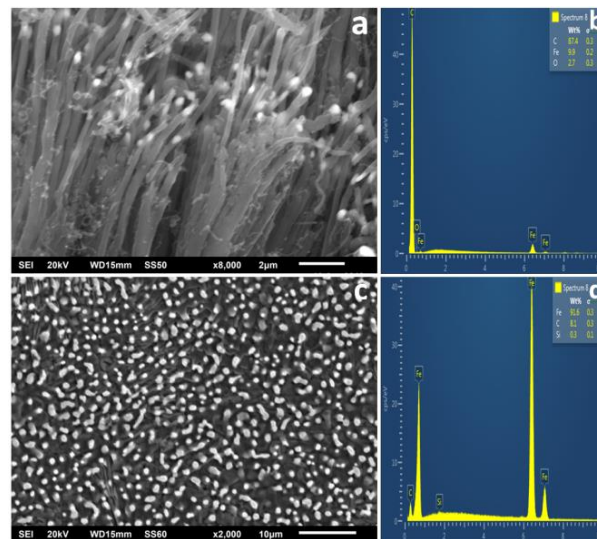


Fig.2. The enlarged SEM image (a) and the respective EDX spectrum (b) of the free-poured nanopowder removed from the area 2, in **Fig.1**. The enlarged SEM image (c) and the respective EDX spectrum (d) of the same area after removal of the synthesized product.

nano dimensions of the droplets and the topology of their arrangement on the physical surface of the substrate. The precise SEM-EDX analyses illustrated in **Fig. 2 a-d** gives a single-valued explanation of why the surface of the ground iron plate became, in the above synthesis conditions, a catalytically activated source of Fe atom nanoclusters for the nucleation and growth of the above-described CNTs doped with the Fe atom clusters. The separate questions are the reasons and ways of transformation and self-organization of the flat surface of the bulk plate iron substrate to the observed catalytically activated surface, nanopatterned with the iron nanodroplets (nanoclusters). In order to shed more light on these questions, the additional experiments were conducted in two reactors working in different modes to study the short-time (30 min) interaction between the ethanol pyrolysis gaseous products and the substrate surface at 1200°C . One plate-substrate sample was exposed in the closed-loop reactor in the mode of recirculation of pyrolysis products at a pressure higher than atmospheric. The second sample was exposed in the open reactor in the mode of flowing gaseous reagents at atmospheric pressure. This effort was motivated by our supposition on the role of interaction between hydrogen and the substrate top layers leading to subsequent transformation to the above-described catalytically activated nanopatterned surface.

Fig.3. a-d show the SEM images of the characteristic morphology of the surfaces and the corresponding EDX spectra of the two Armco-iron plate substrates after a short-time exposure at $1200^{\circ}\text{C} - 0.5\text{h}$: one, in the open-cycle reactor in the mode of flow of the ethanol vapor pyrolysis gaseous products (**a, b**), and the second, in the closed-loop reactor in the mode of recirculation of the ethanol vapor pyrolysis gaseous products (**c, d**). It is obvious that after the short-time exposure at 1200°C in the open cycle reactor the substrate surface has a typical microstructure

characteristic to that of high-temperature gas corrosion interaction with a polycrystalline bulk metal, where different grains with different orientations of crystallographic planes on the surface have different patterns of “corrosion etching” (**Fig. 3. a**). The products of the synthesis are not practically observed except the single spheroidal iron clusters covered with carbon nano-shells (see the inserted enlarged SEM image of the marked area in **Fig. 3. a**). The latter is confirmed by the presence of Si and Mn peak tracks (the alloying elements of Armco iron), together with the low-intensity peak of C in the EDX spectrum taken from the marked area in **Fig. 3.b**. The comparison of the latter to the SEM images taken from the plate-substrate after exposure in the closed-loop reactor in the mode of recirculation of pyrolysis gaseous products (**Fig. 3.c, d**), clearly shows a considerable difference in the morphology and composition of the samples’ surface.

Namely, in this case, on the surface of the substrate a product of the synthesis is observed in the form of close-packed spheroidal clusters of Fe covered with the nanoshells build of pyrocarbon atoms. Corresponding EDX spectrum, taken from the top surface of the initial stratum of the synthesized product (**Fig. 3.d**), shows only the intensive peaks of C and Fe. The fact that the Si and Mn peaks disappear indicates that the thickness of the observed stratum is more than 100 nm, and consequently, the substrate matrix does not contribute to the formation of the spectrum, opposed to the previous case.

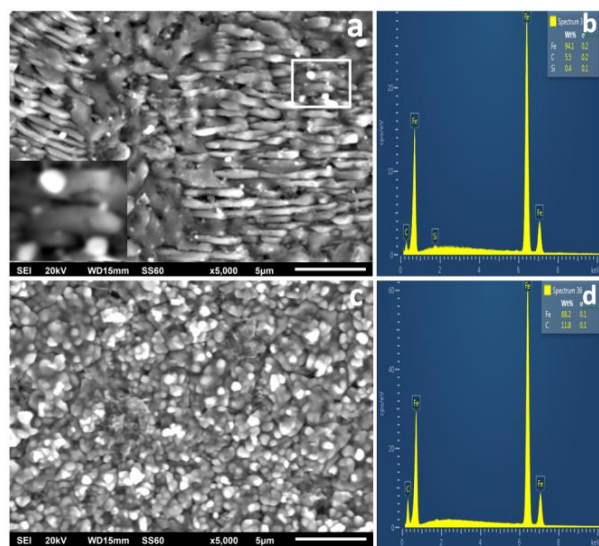


Fig. 3. SEM images and the respective EDX spectra of two Armco iron substrates after their exposure at 1200°C - 0.5 h: one, in the open-cycle reactor in the mode of flow of the ethanol vapor pyrolysis gaseous products (a, b), and the second, in the closed-loop reactor in the mode of recirculation of the ethanol vapor pyrolysis gaseous products (c, d).

The analogous experiments performed in the closed-loop reactor, in absence of oxygen (at partial pressure $\sim 10^{-25}$ torr), lead to exactly the same results described above. Therefore, we may suppose that the presence of hydrogen in the pyrolysis gaseous products

during high-temperature interaction with the surface of a solid-state plate-substrate plays a considerable role in the initial stage of the core-shell-type CNFs formation mechanism. The latter provides a suitable condition for transformation of the plate substrate’s surface (subsurface) bed to the catalytically active surface, patterned with the iron nanodroplets (clusters).

Based on the obtained experimental results and the above assumption, the formation mechanism of CNTs (or CNPs) doped with Fe atom clusters directly on the surface of Fe plate-substrate may be schematically illustrated by the sketch shown in **Fig. 4.a-c**. Because of a dissociative chemisorption of H_2 , diffusion rate and solubility of hydrogen atoms in the superficial layers of the plate-substrate during the interaction of ethanol pyrolysis gaseous products (C, H_2 , O) with the metallic substrate surface at high temperatures, a protonated bed of certain thickness is formed on the plate-substrate (**Fig. 4. a**). The increase in iron crystal lattice parameters, caused by penetration of hydrogen atoms (protons) into the lattice, provides distending of the bed, and thus, a formation of compressive stresses from the surrounding conducting non-protonated areas. Relaxation of the constrained conditions of the protonated bed, in which a weakening of atomic bonds also occurs, facilitates the structural transformation of the 2D continuous medium to discrete 3D-structured magic atom-number nanoclusters and the coalesced cluster aggregates (**Fig. 4.b**). Spontaneous coalescence of these aggregates in giant Fe atomic clusters (at comparatively low temperatures), or their fusion and formation of nanodroplets (at comparatively high temperatures), provides the patterning of the substrate surface. The latter serves as the statistically uniformly distributed catalytic centers of CNF’s nucleation and growth. Consequently, the second and the last stage of growth is a nanoparticle-guided nucleation and growth through the VLS (**Fig. 4.c**) or VS growth mechanisms, when one cluster (or nanodroplet) nucleates one CNF (CNP, CNT) nanoparticle, and the size of each nucleation center on the substrate surface determines the basic size of the core-shell-type CNF nanoparticles doped with the Fe atom clusters.

In this synthesis it is assumed that gaseous carbon (ethanol vapor pyrolysis product) gets directly to nucleation at the interface between Fe nanodroplet and substrate (**Fig. 4.c-1**) and assembled to a multi-walled CNT on the solid surface of the substrate under droplet (**Fig. 4.c-2**). It is obvious that only a diameter of the CNT can be derived from the size of a nanodroplet, while the length of the CNT, as of the tail of the droplet lifted from the substrate surface, depends on the concrete thermodynamic and kinetic parameters in the reactor (**Fig. 4.c-3**), that varies from the values close to zero to some tens of microns.

The reliability of the suggested scheme of a direct synthesis of core-shell-type CNTs (or CNPs) doped with Fe atom clusters on the iron plate-substrate is demonstrated by the results obtained in our special model experiments (see **Fig. 2** and the SEM image

inserted in Fig. 4. C-4), and is in a good agreement with the universal models of nucleation thermodynamics and growth kinetics proposed by G.W. Yang in [10] for 1D nanostructures.

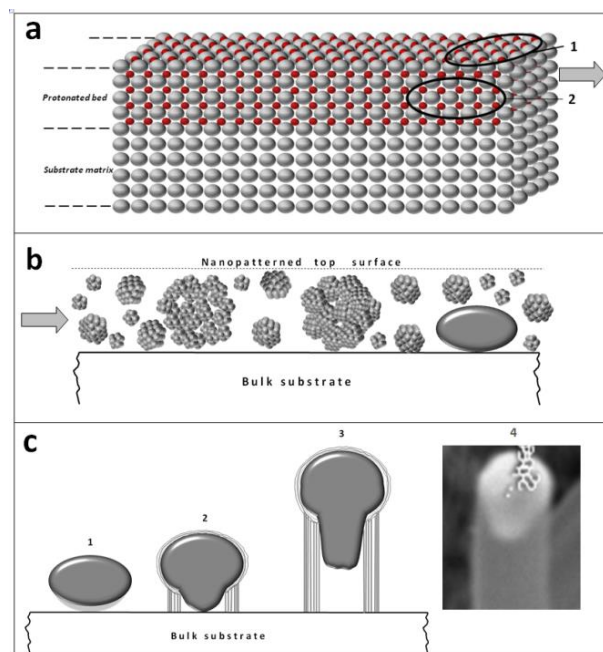


Fig. 4. (a) A sketch of hydrogen distribution in the substrate surface and subsurface: 1. Surface acts as an H-trap. 2. Sub-surface sites (protonated bed). (b) A sketch of transformation of the protonated bed to nanopatterned top surface of the substrate. (c) A schematic illustration of main stages of nucleation and growth kinetics of the CNT doped with the Fe clusters:

1. CNT nucleation on the interface between Fe nanodroplets (clusters) and the substrate.
2. The nanodroplet is lifted in the growing CNT nucleus and subsequently incorporated in a pyrocarbon shell.
3. The grown cluster maintained on the CNT's tip.
4. The insert SEM image of the synthesized at 1200°C single CNT, doped with the Fe atom cluster.

Conclusion

The results of our observations presented in this work lead to the following conclusions:

All the cases considered in this study confirm that hydrogen plays a determining role in the realization of structural mechanism of the direct synthesis of the core-shell-type Fe atomic clusters-doped CNFs on the surface of iron plate substrates, without preliminary deposition of catalyst materials (nanopowder or film state catalyst precursors), via interaction with the products of ethanol vapor high-temperature pyrolysis in the closed-loop reactor.

The mechanism of formation of Fe atomic clusters-doped CNFs on plate-substrate surfaces may be represented as a process, the first stage of which is a protonation of the substrate subsurface layers caused by diffusion of hydrogen atoms, facilitating the formation of 3D nano-groups of Fe atoms assembled in the characteristic magic atom-numbers clusters, depending on the thermodynamics of the metal. The spontaneous coalescence of these clusters into giant Fe-clusters at

comparatively low temperatures and formation of iron nano-droplets at comparatively high temperatures results in the formation of a nano-patterned surface with the uniformly distributed catalytic centers of nucleation of CNFs. The second stage of the process is a nanoparticle-guided growth through the VLS (or VS at low temperatures) mechanisms in which the one cluster provides a nucleation of only one CNF particle so that the sizes of the nucleation centers determine the basic size of the core-shell-type CNF nanoparticles with the incorporated Fe atomic clusters.

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