

Symmetry-related growth of carbon nanocoils from Ni–P based alloy particles

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Nanocrystalline Ni–P and Ni–X–P (X=W,Co,Cu) alloys deposited on the surfaces of SiC whiskers were evaluated on their roles in the catalysis growth of carbon nanocoils during thermal pyrolysis of acetylene. Experimental results indicated that the Ni–P and Ni–W–P systems were effective in catalyzing the growth of carbon nanocoils with varying chirality. Single-particle related growth of the single- or multihelixed carbon nanocoils was found, which suggests that these nanocoils have specific growth characteristics closely related to the symmetroid or surface symmetry of the catalyst particle. © 2004 American Institute of Physics. [DOI: 10.1063/1.1689734]

I. INTRODUCTION

Carbon nanocoil, as one of the important carbon nanostructures, has attracted much attention due to its potential applications as electromagnetic wave absorber and tunable micro- or nanodevice, and so on.^{1–3} To date, various catalysts for catalytic growth of carbon nanocoils have been developed. They include Ni, Au, Ni/Au, Fe/SnO₂, and Fe/In₂O₃.^{1,3} Chen^{4,5} and Wen⁶ also found that P and S impurities introduced in the Ni catalyst were favorable for the growth of carbon nanocoils/microcoils. Several formation mechanisms were proposed by Amelinckx,⁷ Nakayama,^{3,8} and Motojima.^{1,9} In our previous work,¹⁰ we found the formation of carbon nanocoils when we used a nanocrystalline Ni–P alloy catalyst to synthesize carbon nanotubes and nanofibers. Further experiments indicated that Ni–P based ternary alloys could also catalyze the growth of carbon nanostructures. As a large-scale and reproducible synthesis of carbon nanocoils is of great importance for the potential applications of carbon nanocoils, we report here the formation of various carbon nanocoils through single-particle catalysis with Ni–P based alloys as the catalysts. Growth mechanisms related to the symmetroid of the catalyst particle were discussed.

II. EXPERIMENT

SiC whiskers (10–30 μm in length and 0.1–1 μm in diameter) were sensitized in a SnCl₂ solution and then activated in a PdCl₂ solution. The preparation of Ni–P based alloy catalysts (Ni–12P, Ni–13.9W–10.5P, Ni–34.6Co–5.5P, Ni–13.1Cu–5.6P, wt %) on the surfaces of the SiC whiskers was carried out by electroless plating,^{11–14} and then by a crystallization of the amorphous nanoislands¹⁰ in inert atmosphere (N₂ or Ar) before a pyrolysis reaction. A silica

plate coated with the alloy/SiC powders was put in a quartz tube, which was heated at 500–950 °C (for 30–60 min) for the crystallization and heat treatment of the Ni–P based alloys. This step was designed to form preferred nanoislands on the surfaces of the ceramic whiskers. After the preparation of catalytic particles, the pyrolysis of C₂H₂ (10–30 ml/min) at 500–700 °C for 30–60 min was conducted with N₂ or Ar (at a flow rate of 200–500 ml/min) as the dilute gas. The products were examined with transmission electron microscope (TEM) (JEM 2010F).

III. RESULTS AND DISCUSSION

In addition to carbon nanotubes and/or nanofibers found in the pyrolysis products (Table I), not all of the Ni–P based alloy catalysts (whether binary or ternary) have the ability of catalyzing the growth of carbon nanocoils. Ni–P and Ni–W–P alloys had such ability but Ni–Co–P and Ni–Cu–P alloys did not. Single- and multihelixed carbon nanocoils (up to 5% in total) were observed in the former two catalysis systems.

A close examination of these helixed carbon nanocoils revealed that the growth of these nanocoils was in fact a symmetry-related process. From the single-helixed carbon nanocoils shown in Fig. 1, it could be found that each catalyst particle had specific symmetroids (symmetric surfaces). It could be inferred that these symmetroids were mainly responsible for an ordered anisotropic precipitation of carbon atoms on the surfaces of the corresponding particle, and thus a formation of the corresponding nanocoil. That is, at the pyrolysis temperatures, three-dimensional movement of the catalytic particle and a continuous extrusion of carbon atoms along the symmetroid made it possible to grow the single-helixed nanocoils. The slight difference in the symmetroid [Figs. 1(a), 1(b), 1(c), and 1(d)] could result in difference in the chirality of these single-helixed nanocoils. Growth of the earlier single-helixed nanocoils partly followed the Yang's two-dimensional model,⁹ which used some symmetry sur-

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TABLE I. Summary of carbon nanocoils grown in different Ni-P based catalysis systems.

Alloy	Nanocoils?			
	Single-helixed	Double-helixed	Triple-helixed	Tetrahelixed
Ni-P	√	√	√	√
Ni-W-P	√	√	√	...
Ni-Co-P
Ni-Cu-P

faces of a catalyst particle to explain the incorporation and precipitations of carbon atoms along different directions.

Once the as-formed symmetroid could meet the requirement for closely spatial interaction of the nanocoils grown from the corresponding catalyst particle, single-helixed nanocoils grown from the symmetry surfaces of the particle would interact together to form double-helixed carbon nanocoils. This could be verified by the double-helixed carbon nanocoils shown in Fig. 2. The symmetroid included nancone surfaces [Fig. 2(a)], tetragonal surfaces whether flat or not [Figs. 2(b), 2(c), and 2(d)]. Slight difference in the symmetroid also made it possible to grow double-helixed nanocoils made up of either circular nanofibers [Figs. 2(b) and 2(c)] or flat nanoribbons [Fig. 2(d)]. As for the triple-helixed nanocoils [Figs. 3(a) and 4(b)] and tetrahelixed nanocoils [Fig. 3(c)], nonspherical catalyst particle having certain symmetric surfaces could also catalyze the growth of these multihelixed nanocoils. This was similar to Chen's finding that single-particle catalyzed growth of as many as six carbon fibers from six crystal faces of a hexahedral Ni catalyst was feasible.¹⁵ However, for the multi-element catalysis systems here, the interaction of neighboring single nanocoils should be more complex and the structural characteristics (including symmetric surfaces and their variation with alloying element) of the catalyst particle needs to be further investigated. The carbon nanocoils synthesized here tended to show a non-graphitic structure (Fig. 5), which suggests that further annealing¹⁶ at elevated temperatures is needed.

It should be mentioned that the growth of the earlier nanocoils mainly depended on the heat-treatment and alloy system of the alloy catalysts. For example, in the Ni-P alloy system pretreated at temperatures above 700 °C [Figs. 6(a) and 6(b)] quite a few of single-helixed carbon nanocoils could grow at a pyrolysis temperature of 525 °C (Fig. 1). But in the Ni-P alloy system pretreated at a lower temperature

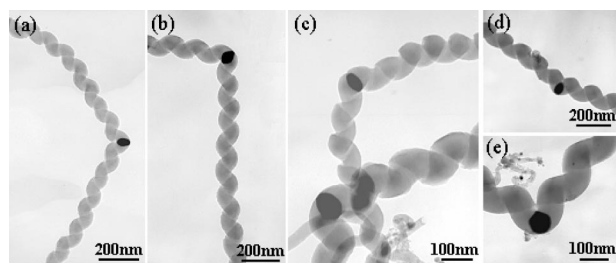


FIG. 1. (a)–(e) Single-helixed nanocoils observed in the Ni-P system. The encapsulated particles had different symmetroid, which resulted in the formation of different chirality in the corresponding nanocoil.

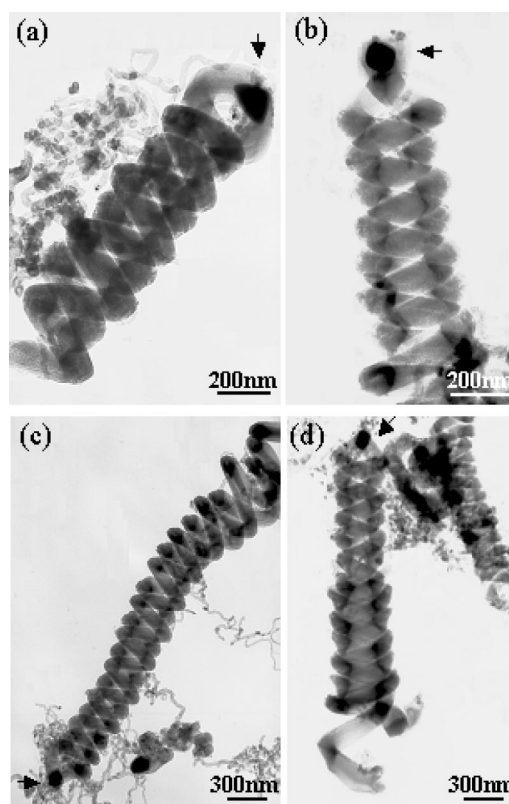


FIG. 2. (a)–(d) Double-helixed nanocoils observed in the Ni-W-P system. The arrows point to the catalytic particles showing different symmetroid.

such as 550 °C, single-helixed carbon nanocoils rarely formed and only multihelixed nanocoils could grow.

Compared with the originally deposited Ni-P nanoislands¹⁰ or heat-treated nanoparticles [Fig. 6(a)], only a few of catalyst particles were found on the whisker surfaces (after a pyrolysis reaction) because the catalyst nanoparticles could diffuse away with carbon atoms from the whiskers during the growth of carbon nanostructures. A close examination of the nanoparticles left on the whisker surfaces also revealed that with a pretreatment the catalyst particles participating in the pyrolysis reaction tended to have a nonspherical surface favorable for the formation of carbon nano-

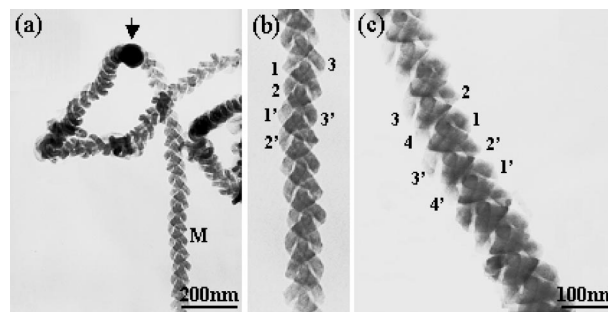


FIG. 3. Multihelixed carbon nanocoils observed in the Ni-P system. (a)–(b) triple-helixed nanocoils grown from one catalyst particle, and (c) tetrahelixed nanocoils. The arrow in (a) points to the catalyst particle showing a nonspherical shape. (b) is a higher magnification of region *M* marked in (a). The numbers in (b) represent three nanoribbons that formed the triple-helixed nanocoils. The numbers in (c) represent four nanoribbons that formed the tetrahelixed nanocoils.

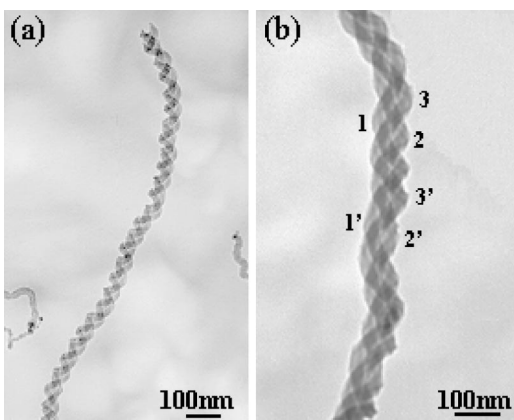


FIG. 4. Multihelixed carbon nanocoils observed in the Ni–W–P system. (a) Double-helixed nanocoils, and (b) triple-helixed nanocoils. The numbers in (b) represent three nanoribbons that formed the triple-helixed nanocoils.

coils [Fig. 6(b)]. Whereas, without a pretreatment most of the relic catalyst particles tended to have a spherical surface unfavorable for the formation of carbon nanocoils, and thus the corresponding yield of nanocoils was lower [Fig. 6(c)]. The earlier results suggest that heat treating the catalyst particles to specific shapes (i.e., regular symmetroid) should be one of the important ways to synthesize carbon nanocoils.

It has been generally accepted that transition metals of VIII group and their alloys are mainly responsible for the catalytic growth of carbon nanostructures. The addition of S, P, Cu, Zn, and Mg elements could adjust the catalytic nature of the active metals and thus change surface adsorption and decomposition of hydrocarbons.¹⁷ Our high-resolution electron microscope (HREM) observations and energy dispersive spectra analyses of the carbon nanostructures and catalyst particles indicated that, in addition to the catalytic ability of Ni nanoparticles which diffused away from the alloy mixtures, Ni–P and Ni–W–P nanoparticles could also serve as the real catalysts for pyrolyzing the acetylene. And it also showed that the carbon nanostructures obtained in the Ni–P

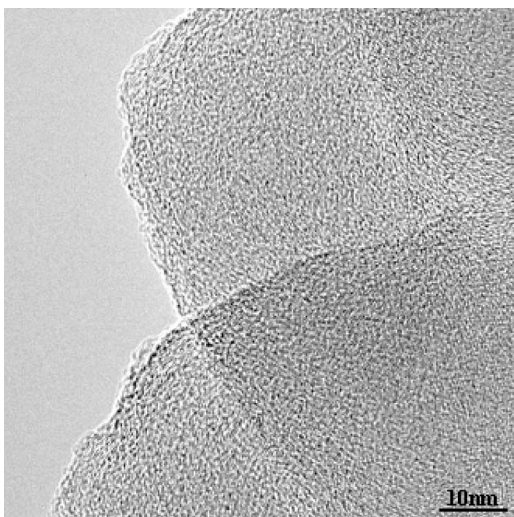


FIG. 5. HREM image of double-helixed carbon nanocoils showing nongraphitic structures.

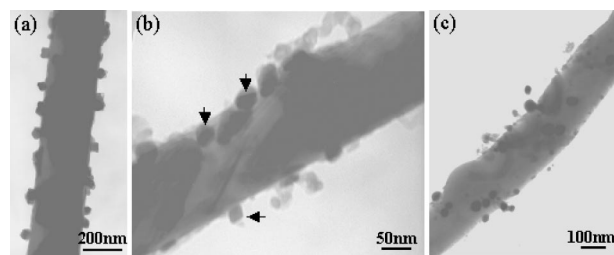


FIG. 6. TEM images of Ni–P nanoparticles. (a) A heat treatment before the pyrolysis reaction could result in the formation of considerable number of nanoparticles having symmetry surfaces. (b) With a pretreatment nanoparticles left on the whisker surface tended to have a nonspherical surface (marked by arrows). (c) Without a pretreatment nanoparticles left on the whisker surface tended to have a spherical surface, which was unfavorable for the formation of nanocoils.

and Ni–W–P systems were much more uniform than those in the Ni–Cu–P and Ni–Co–P systems.

The present work suggests that, at elevated temperatures, only specific Ni–P based alloy systems (i.e., Ni–P and Ni–W–P) could form symmetry particles that were favorable for the growth of helixed nanocoils from the corresponding symmetroid. It can be inferred that, W alloying with the binary Ni–P had not prevented the formation of favorable surface symmetry in the catalyst particle. Thus, regular nanocoils grown from the symmetroid of the catalyst particle could be found. Whereas, for the Ni–Co–P and Ni–Cu–P systems, Co and Cu alloying with binary Ni–P could not help to form favorable symmetroid in the catalyst particle, which would result in unfavorable anisotropic precipitation of carbon atoms from the catalytic particles. As a result, with the Ni–Co–P and Ni–Cu–P system, it was difficult to form single- and multihelixed nanocoils during the pyrolysis reaction.

The diameter of the carbon nanocoils synthesized in the Ni–P system was generally smaller than that synthesized in the Ni–W–P system because the as-deposited Ni–W–P nanoislands here had a relatively large diameter than the Ni–P nanoislands had. This suggests that by optimizing the appropriate deposition process the diameters of these carbon nanocoils could be adjusted. It could be expected that, for a specific alloy system, controlling surface morphologies of the catalysts particles by using appropriate pretreatment and temperatures would be effective for obtaining carbon nanocoils with varying chirality. And the yield of carbon nanocoils is expected to increase with further optimizing the quantity of preferred catalyst particles and the pyrolysis parameters.

IV. CONCLUSION

With Ni–P based binary and ternary alloys as the catalysts, catalysis mechanism on a chemical vapor deposition growth of carbon nanocoils was examined. From single-helixed nanocoils to multihelixed nanocoils, the growth of nanocoils mainly depended on the symmetroid of the catalyst particle. Such a relationship between the symmetry and the chirality/coiling made it possible for potential controllable synthesis of various carbon nanocoils.

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