13 August 2002

Chemical Physics Letters 362 (2002) 135–143

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

Dispersing and coating of transition metals Co, Fe and Ni on carbon materials

Ziyi Zhong [a], Binghai Liu [b], Lianfeng Sun [a], Jun Ding [b], Jianyi Lin [a,*], Kuang Lee Tan [a]

[a] *Department of Physics, Surface Science Laboratory, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260*

[b] *Department of Materials science, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260*

Received 7 August 2001; in final form 25 June 2002

Abstract

Interaction between transition metals Co, Fe and Ni and carbon materials, such as multi-walled carbon nanotubes (MWNTs), single-walled carbon nanotubes (SWNTs), activated carbon (AC) and layered graphite (LG), has been investigated at high temperatures. Complete wetting for AC, partial wetting for MWNTs, and almost no wetting for SWNTs and LG have been observed, respectively. It is found that the defects in the carbon materials play a key role in the interaction. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Carbon nanotubes (CNTs), which were first discovered by Iijima [1], have attracted intense interest in recent years because of their novel one-dimensional structure and expected electronic and magnetic, mechanical and gas adsorption properties. To fabricate nanoscale devices based on carbon nanotubes with improved electronic properties and functions, several important techniques have been employed and developed. These techniques include the designed doping of other elements such as boron and potassium in the layer graphitic structure of CNTs [2,3], filling of metallic elements into the empty channel of CNTs by arc-discharge method [4] and wet chemistry method [5–8], and a recently reported two-step catalytic reaction that results in a high-yield synthesis of GaN nanowires encapsulated inside CNTs [9], coating of metals on the outer walls of CNTs [10,11], and even directly using CNTs as template to prepare wire-structured GaN [12] and carbide nanorodes [13]. However, in some cases these methods can only meet with limited success. For examples, the conventional arc-discharge technique is successful only for the encapsulation of rare earth metals, but to the transition metals such as Fe, Co and Ni, it is not successful in producing the completely filled nanotubes with macroscopic quantities [14]. By wet chemistry method, the abundance of completely filled structures is also low and their production is difficult to control

---

[*] Corresponding author. Fax: +65-874-6126.
E-mail address: phylinjy@nus.edu.sg (J. Lin).

PII: S0009-2614(02)01044-8

[7,14,15]. To get good wetting effect, it usually demands the chosen materials have a surface tension of less than 100–200 N/m. There are only limited materials that can match the above wetting criteria [16,17].

Apart from the above mentioned and potential applications for CNTs, carbon supported catalysts have been found to be efficient for many catalytic reactions such as hydrogenation reactions [18,19]. However, to date, we have found that little attention has been paid to the interaction of carbon materials such as CNTs with transition metals, especially in high temperature range, though it is a very important aspect in fundamental research. In this study, four typical carbon materials, namely MWNTs, SWNTs, AC and GC, and three transition metals, Co, Ni and Fe have been selected to investigate the interaction between the metals and carbon materials. The interaction has found to be determined by the defects in the carbon materials.

2. Experimental

Nitrates of iron, cobalt, nickel and magnesium were obtained from Aldrich, graphite powder and *activated carbon from Merck*. All of the chemicals were used as received.

The preparation of MWNTs by decomposition of methane over Ni/MgO catalysts at 700 °C was described in literature [20,21]. The produced MWNTs were treated with concentrated sulfuric acid to dissolve metallic catalyst, rinsed with distilled water and dried at 300 °C for 4 h in air. The preparation of SWNTs was described in our recent Letter [22] using a $Mo_{0.01}Co_{0.05}Mg_{0.94}O$ catalyst and a mixture reaction gas of H_2 and CH_4 with a molar ratio of 1:4 and a total flow rate of 250 cm^3/min. The prepared SWNTs were first treated with nitric acid and washed with distilled water, then dried at 400 °C in air for 3 h to remove the amorphous carbon. The content of the SWNTs in the treated sample was evaluated to be 70–80% according to a temperature-programmed oxidation measurement. The impurities in the above-treated SWNTs are residual metal Co, graphitic particles and MWNTs. The metals Fe, Co and Ni were prepared by decomposition of their nitrates at 600 °C in air for 1.5 h, followed by reduction in hydrogen at 600 °C for 1 h.

The prepared metals Fe, Co and Ni were physically mixed with the MWNTs or other carbon materials, respectively, and heated in highly purified argon in a quartz tube with a flow rate of 5–10 ml/min. The weight loss after heat treatment was usually less than 5–8 wt%. The microstructure and the morphology of the annealed products were observed employing a JEM-100CX transmission electron microscope. X-ray diffraction (XRD) scans were obtained using a Bruker D8 Advance diffract meter with a Cu target and a scanning step of 0.05°/s for conventional measurements. Slow scan mode was also used to measure precisely the strongest X-ray diffractions of metallic Co, Fe and Ni with a step size of 0.001°/s. In situ XRD measurement for Fe–MWNTs system at different temperatures was conducted in argon gas within a HTK 16 high-temperature chamber. The heating rate was 30 °C/min. Each XRD pattern was recorded after the chosen temperature had been reached and stabilized for 30 min. All the samples for XRD measurement were pressed into thin flakes.

3. Results and discussion

The XRD patterns for metal (Co–, Fe– and Ni)–carbon systems have been measured before and after the heat-treatment in Ar gas at 1000 °C for 10 h. The interaction was shown to depend very much on the type of the carbon materials. MWNTs and activated carbon behave alike whereas LG and SWNTs are very different. As shown in Fig. 1, after heating there is only a slight decrease in diffraction intensity for the Co(1 1 1) diffraction in Co–LG and Co–SWNTs systems (Figs. 1a–d, respectively), an obvious decrease in intensity for the Co diffraction in Co–MWNTs system (Figs. 1e and f), but an almost complete vanish of the diffraction peak for Co in Co–AC system. LG seems to be the most inert in the interaction with the metals. Although not shown here, very similar phenomena have been observed for Ni and Fe.

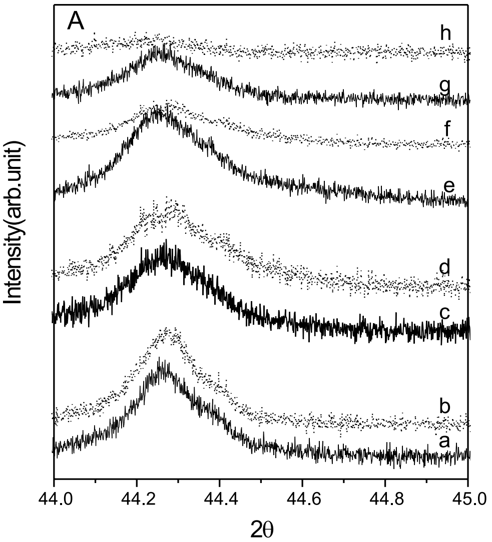

Fig. 1. The slow scans of the Co(1 1 1) diffraction for various metal–carbon material systems before and after heat-treatment at 1000 °C for 10 h in Ar gas: Co–LG system (a and b); Co–SWNTs system (c and d); Co–MWNTs system (e and f); Co-AC system (g and h).

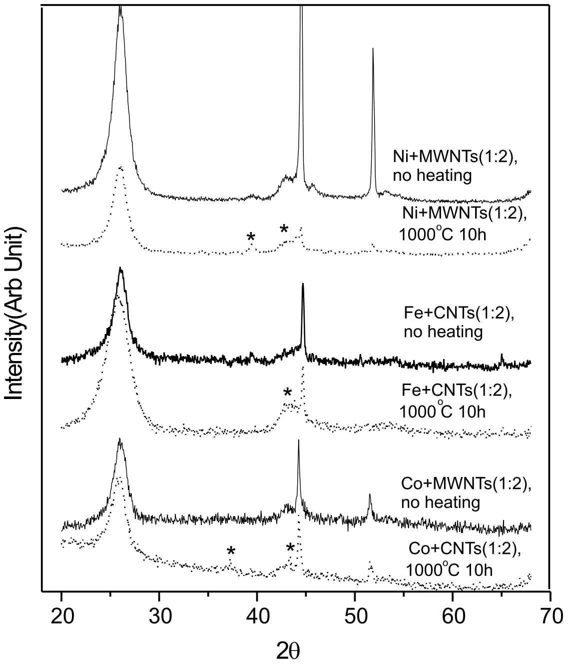

Fig. 2. XRD patterns of Co–, Fe– and Ni–MWNTs systems before and after heating at 1000 °C for 10 h in argon.

The changes in the diffraction intensity of the metals after the heat-treatment of the metal/C mixture directly reflect the strength of the interaction between the metals and the carbons, because the decrease in intensity is caused by the dispersing of the metal particles and/or the transformation of the metals to other phases (such as metal carbides). Obviously, the interaction between the metals and various carbon materials follows the order: metals–AC $\gg$ metals–MWNTs $>$ metals–SWNTs $>$ metals–LG.

The metal–MWNTs systems have been selected for further investigation. Fig. 2 shows the XRD patterns for Co, Fe and Ni mixed with MWNTs before and after heated at 1000 °C. From the two Co patterns at the bottom of Fig. 2, we can see, after the heat-treatment, a hump appears near the strongest diffraction peak of the fcc cobalt at $2\theta = 44.24°$. At the same time, two new small peaks (marked with an asterisk) are identified, with the first one being centered at $2\theta = 42.5°$ corresponding to a *d*-spacing of 2.13 Å, and the second one at $2 = 37.3°$ corresponding to a *d*-spacing of 2.41 Å, all of which can be ascribed to the formation of trace carbide Co_2C. For Ni–MWNTs system (two top patterns in Fig. 2), the appearance of a new small diffraction peak at $2\theta = 39.4°$, and a hump near $2\theta = 45°$ indicate the formation of nickel carbide Ni_3C referred to ASTM card 72–1467. Actually we observed these peaks in the samples heated at 750 °C for 10 h too, showing the nickel carbide can be formed at lower temperatures. For Fe–MWNTs system a huge hump centered at about $2\theta = 43°$ can also be observed after heating at 1000 °C for 10 h (Fig. 2). But it is still not very clear if the new compound is Fe_3C (ASTM card 75-910), or Fe_7C_3 (ASTM card 75-1499, and [23,24]), or ε′-carbide ($Fe_{2.2}C$), or just a solid solution of carbon that has incorporated in iron. Because the diffraction peaks of these compounds usually overlap in this range, it is not easy to discern them in the XRD pattern. To better understand this interaction process for Fe–MWNTs system, we carried out an in situ XRD measurement by heating the Fe/MWNT mixture (1:2 by weight) in Ar from room temperature to 1000 °C, and the XRD patterns are shown in

Fig. 3a. The small peak at $2\theta = 35.3°$ (marked with an asterisk) for the samples heated between 400–800 °C is ascribed to the formation of trace Fe_3O_4 (ASTM card 72-2303). The Fe_3O_4 may originate from the oxidation of Fe by trace of oxygen in the system. Unfortunately from this in situ XRD measurement we still do not observe any other diffraction peaks of the iron carbides such as Fe_3C and Fe_7C_3 than the hump peak near $2\theta = 45°$. The missing of these diffractions excludes, at least, the possibility that the carbides were formed as intermediates but decomposed at higher temperatures.

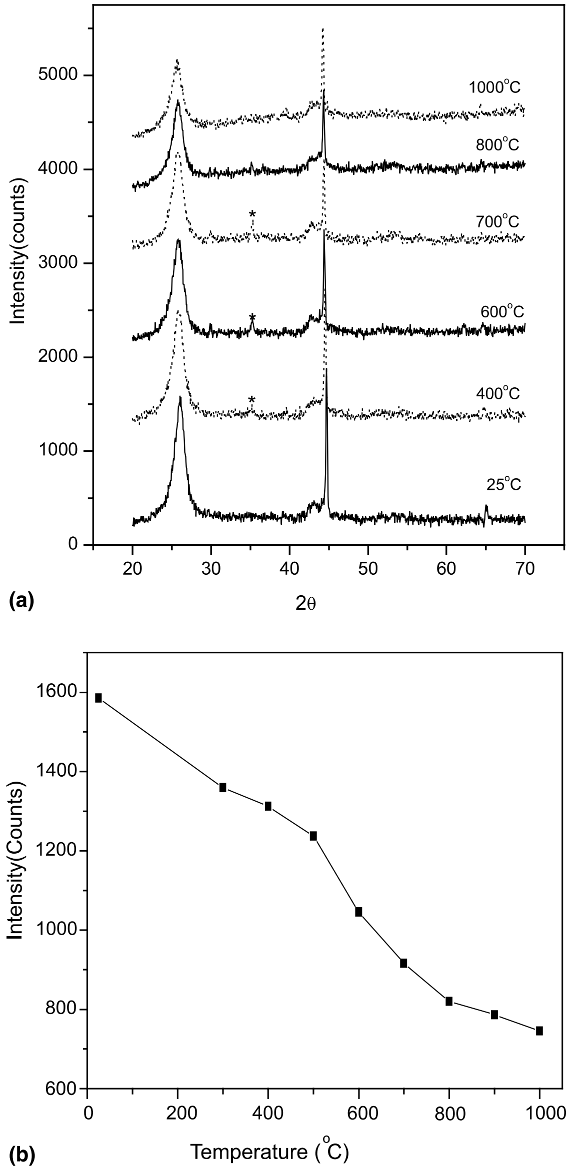

Fig. 3. (a) XRD patterns for the Fe–MWNTs system with a weight ratio of Fe:MWNTS = 1:2 obtained from an in situ measurement; (b) the intensity of (1 1 1) diffraction of the metallic iron in (a) vs. heating temperatures.

It has been reported that Co, Fe and Ni usually form non-stoichimetric and interstitial solid solutions with carbon. Some metastable phases were observed [25,26], but the formation of these transition carbides is still a disputable issue. It seems to depend strongly on reaction conditions such as precursors, atmosphere, particles size, and so on. For example, nanosized nickel particles reacted with some organic carbon sources to form Ni_3C at 200 °C, but this carbide decomposed at temperatures above 300 °C [27]. In other reports [28] Ni_3C could be formed at the front side of Ni–Cu catalyst particles at 550 °C, or on Nickel electrode above 900 °C [29]. In our case, the Co_2C and Ni_3C were observed by XRD measurement after high temperature treatment, clearly indicating the involvement of a covalent bonding process between MWNTs and metal atoms. In the case of Fe–MWNTs system, though we cannot determine what kind of carbide phase was formed, the observation of a hump near $2\theta = 43°$ should be connected to a bonding process between the Fe particles and the MWNTs, at least at the MWNTs–Fe interface. As mentioned above, the incorporation of carbon into iron can result in the formation of interstitial solid solution.

In addition to the carbide formation, the decrease of the diffraction intensity after high temperature heating may also be caused by the decrease in the size of metal particles. Figs. 2 and 3 clearly show that the dispersion extent of the metal particles increases with the annealing temperature. We may monitor this interaction process by simply observing the change in intensity of the X-ray diffraction of these metals. Fig. 3b shows the intensity of the strongest X-ray diffraction of metallic iron changes with the annealing temperature. Clearly the dispersion extent of the iron particles almost increases linearly with the annealing temperature. The dispersion process has been more clearly observed by TEM measurement.

Fig. 4a shows a TEM image of the metal Co after reduction. It is seen the particles are in micrometer scale and are crystallized very well. After heated with MWNTs at 1000 °C for 10 h, most of the cobalt particles were highly dispersed, and some of them coated on the surface of MWNTs (Fig. 4b). From the TEM observation we evaluated that the content of the coated MWNTs is about 10–15% out of the total MWNTs. The coated Co particles are in the range of 30–50 nm, and most of them are disconnected to each other. Fig. 4c is a magnified image of Fig. 1b. From it we can still discern the empty channel structure in MWNTs. In our TEM measurements, we never found any carbon tubes that are filled with cobalt particles, indicating this annealing method only leads to the dispersion as well as coating of Co particles on the surface of MWNTs. Definitely this is related to the fact that the annealing temperatures are much lower than those of the melting points of metals Co, Fe and Ni.

Actually in each sample after heat-treatment we always observed three forms of cobalt particles, namely the big Co particles that had not been dispersed yet, the dispersed and the coated cobalt particles. There are several ways to promote the interaction between the cobalt particles and MWNTs. We tried to increase the annealing time

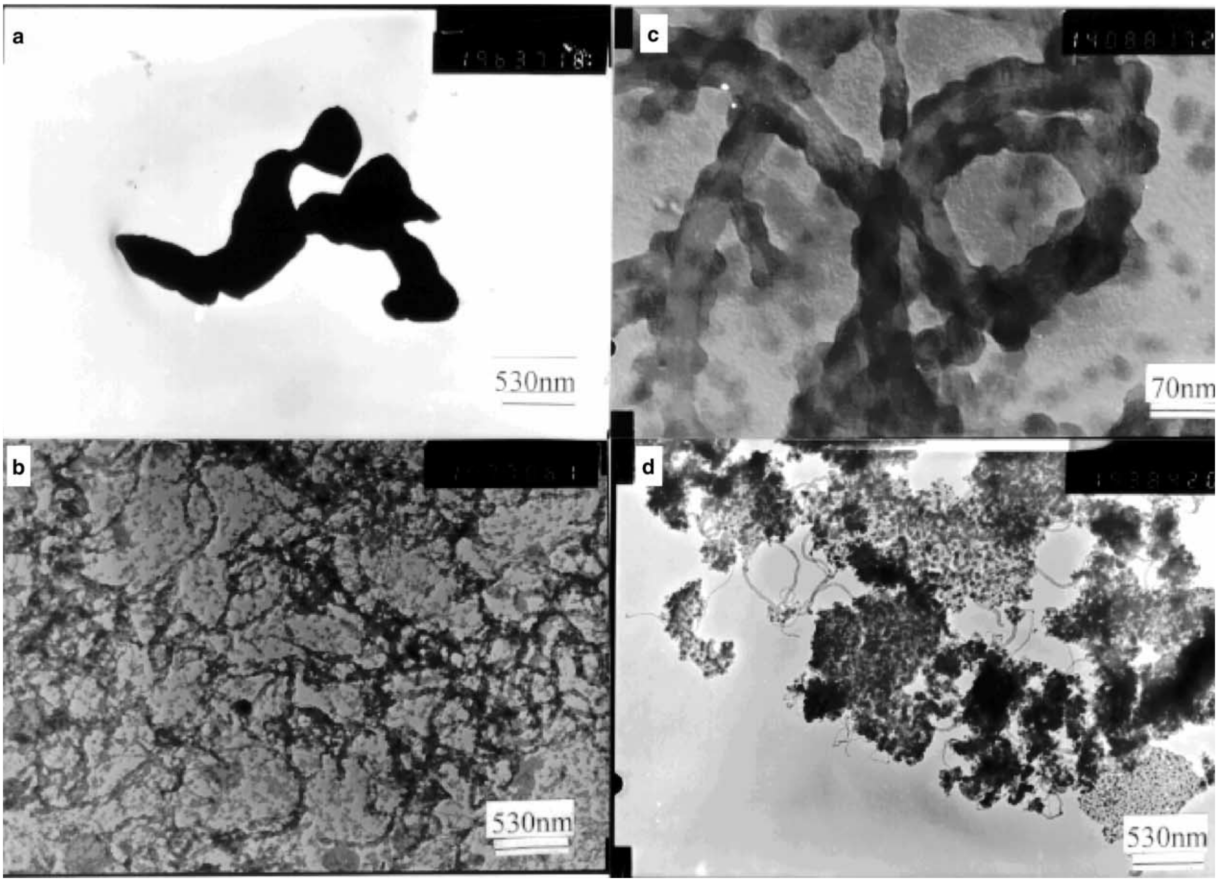

Fig. 4. TEM images of (a) the metallic Co particles from reduction of Co_3O_4 at 600 °C; (b) the coated Co particles on MWNTs in the Co–MWNTs system with a weight ratio of Co:MWNTs = 1:2 and after being heated at 1000 °C for 10 h in argon; (c) magnified of (b); (d) the highly dispersed Co particles in the Co–MWNTs system with a weight ratio of Co:MWNTs = 1:2 and after being heated at 750 °C for 18 h in argon.

or the annealing temperature, or both of them. It was observed by TEM that after heating at 750 °C for more than 20 h or at 1000 °C for 10 h, about 70–80% of Co particles had been dispersed. Heating at lower temperatures or in shorter time resulted in a very incomplete dispersion of Co particles. It seems that heating temperature plays a crucial role in the dispersion effect. When the temperature was below 650 °C, heating even more than 20 h still could not lead to a sufficient dispersion of cobalt. Also, the weight ratio between the metal Co and MWNTs has influence on dispersing effect. When the weight ratio between the metal cobalt and the MWNTs exceeded 1:2, there were still a lot of Co particles in big size after heating at 1000 °C for 10 h. Fig. 4d shows a TEM image of the dispersed Co particles after being heated in 750 °C for 18 h. Its magnified image (not shown here) indicated the black Co particles are uniformly distributed in carbon matrix. The existence of the carbon matrix is similar to our previous observation that the cobalt favors to be encapsulated in carbon [21].

The coated Fe particles on the surface of the MWNTs can form a continuous structure, which is different from the Co. Fig. 5a shows a TEM image of Fe coated on MWNTs that had been heated at 1000 °C for 3 h. The size of Fe particles is in the range of 5–15 nm. But we still can discern the empty channel structure in MWNTs, indicating the coating is still disconnected. After annealing for 10 h at 1000 °C, we found the coated Fe particles had been grown up in size and became connected to each other. At the same time, the

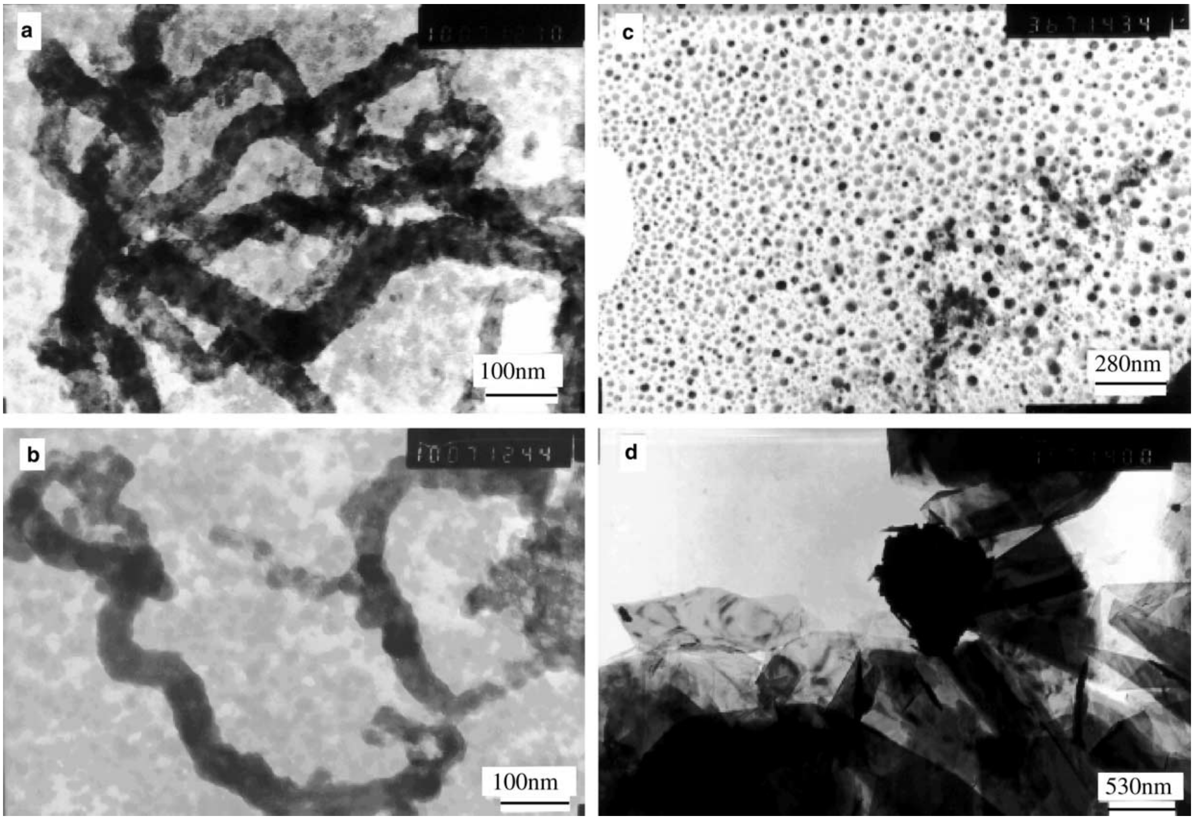

Fig. 5. TEM images of the Fe–MWNTs system (weight ratio Fe:MWNTs = 1:2) heated at 1000 °C in argon for (a) 3 h and (b) for 10 h; (c) the Ni–MWNTs system (weight ratio Ni:MWNTs = 1:2) heated at 1000 °C for 10 h in argon; (d) the Co–graphite mixture with a weight ratio = 1:2 and after being heated at 750 °C for 18 h in argon.

empty channel cannot be seen again, indicating an almost completely continuous coating was reached (Fig. 5b). Near the coated MWNTs, a lot of highly dispersed particles are also observed. It seems that these particles are composed of a mixture of the metallic particles and carbon pieces, or of a hybrid structure. Clearly the heating and the interaction between metal and MWNTs can result in damage of some MWNTs.

Ni can also interact with MWNTs strongly. In our experiments a poorer and discontinuous coating on MWNTs was observed for nickel as compared with the cobalt and iron. However, a much higher extent of dispersion of nickel was observed. Fig. 5c shows a TEM image of the Ni–MWNTs system after being heated to 10 h at 1000 °C. Clearly the nickel particles or their hybrid structure formed with carbon are very uniform in size. Bilaniuk and Howe [30] once reported that the nickel could wet the carbon very readily. Indeed in our experiments, nickel is the most easily dispersed metal compared to Fe and Co.

Co_3O_4, α-Fe_2O_3 and NiO were once used to replace metallic Co, Fe and Ni as precursors to mix and interact with the MWNTs at high temperatures. After being heated at 1000 °C for 2–3 h, XRD results confirmed these metallic oxides had been reduced to elemental metals accompanying a release of carbon dioxide or carbon monoxide. Longer heating will result in a similar dispersion as observed by using the metals as precursors.

Very interestingly from this study we observed the dispersion of metals Co, Fe and Ni on MWNTs after the heat-treatment. Usually heating of metals or their oxides in high temperatures will lead to a marked growth in particle size or aggregation of particles. For example, heating of the metallic Fe or its oxide particles coated on alumina spheres at 400 °C in argon caused a marked growth in particles size. When the temperature was increased to 1000 °C in air, the iron oxide particles would incorporate into the alumina substrate and aggregate together. The aggregation force was so strong even that the alumina spheres were broken into small pieces [31]. In fact we once tried to introduce trace amount of oxygen into the Co–MWNTs system by stopping flowing of argon gas in the quartz tube when heating the Co–MWNTs system at 1000 °C. Consequently an obvious growth in particle size of the cobalt and a partial consumption of the MWNTs were found, so the dispersion of these transition metals is due to their interaction with MWNTs in an inert atmosphere. In other words, the MWNTs can promote the dispersion of the metal particles after heating treatment and stabilize them very well.

In Fig. 5d it is seen the layer graphitic structure and the black metal particles in big size are clearly discerned. There is little Ni particles dispersed and coated on graphite sheets after the heat-treatment. Similar results were observed in the metal–SWNTs system (the image is not shown here). Whereas in metal-activated carbon system, almost all metal particles were highly dispersed after heating at 1000 °C for 10 h.

It is known the ideal graphite consists of layers of hexagonal arrays of carbon in an ABAB-planar stacking arrangement, and the carbon nanotubes can be regarded as rolled graphitic layers having hexagon, pentagon, and heptagon carbon rings as a result of its unique hybridization of sp^1, sp^2 and sp^3 bonding [32,33]. The pentagon and heptagon rings are not as stable as the hexagon rings, and can be regarded as defect sites. For SWNTs, due to the relatively high formation temperature (>900 °C), their defects are very limited. Conversely, the MWNTs possess more defects because of their relative low formation temperature. Compared to the above three carbon materials, activated carbon is poorly crystallized and possesses a lot of structure defects and dangling bonds. Thus, when exposed to the transition metals at high temperatures, the metal atoms should attack these defect sites much more easily to form covalent bonding. Compared to AC and MWNTs, the layered graphite and SWNTs are almost defect free, and therefore they are much less reactive toward transition metals Fe, Co and Ni. So the defect numbers in the carbon materials should determine the strength of the interaction. The more the defect number, the stronger the interaction should be.

We can further understand why the disconnected coating on the MWNTs is firstly formed at the early stage of reaction, probably because there is a distribution of these defect sites on the outer walls of MWNTs. With the increase of annealing time or temperature more and more metal atoms can combine with the carbon atoms, which, in turn, will cause damage to the structure of the MWNTs and produce more and more defects in the wall. Therefore we can observe the dispersion and coating of metal particles on MWNTs. Eventually the growth and connection of coated particles may develop into a continuous coating as observed in Fe–MWNTs system.

Zhang et al. [11] once coated a series of metals on SWNTs by electron beam deposition method. Contrary to our experiments for the metal–MWNTs systems, they observed a continuous coating for Ni and a disconnected coating for Fe. But in our study, almost no coating was observed by TEM on SWNTs. As analyzed above, it is because the heating promoted coating or interaction is strongly dependent on the structure, density and distribution of the defects in the carbon materials.

In summary, the wetting of the carbon materials by the transition metals is determined by the number and structure of the defects in the carbon materials. It is found the graphite sheets and SWNTs are difficult to be wetted, whereas the MWNTs and activated carbon are much easily to be wetted. It also demonstrated that simple annealing of the mixture of transition metals Co, Fe and Ni with MWNTs could result in their dispersion and coating on MWNTs. For Co– and Ni–MWNTs system, a disconnected coating was obtained, and for Fe–MWNTs system, extension of annealing time can change the disconnected coating into a continuous coating. Trace amount of Co_2C and Ni_3C were also confirmed for Co– and Ni–MWNTs system, respectively, after being heated at 1000 °C.

As these metals and their carbides are good magnetic materials [34], their highly dispersed and stabilized states in high temperatures and inert atmosphere may be found with special applications in industry. In addition, the coated CNTs may possess improved electronic, magnetic and chemical properties, so this method can be applied to fabrication of new nanodevices bases on CNTs. Finally, as the CNTs can be used as the novel catalyst support [35], we believe this study will be helpful to the development of the new CNTs-based catalysts.

Acknowledgements

This work is supported by National Science and Technology Board of Singapore (GR6773). The authors would like to thank Madam Loy in Biological Department in National University of Singapore for her assistance in TEM measurements.

References

[1] S. Iijima, Nature 354 (1991) 56.
[2] D.L. Carroll, Ph. Redlich, X. Blasé, J.C. Chalier, S. Curran, P.M. Ajayan, S. Roth, M. Rühle, Phys. Rev. Lett. 81 (1998) 2332.
[3] C. Zhou, J. Kong, E. Yenilmez, H. Dai, Science 290 (2000) 1552.
[4] C. Guerret-Piecourt, Y.L. Bouar, A. Loiseau, H. Pascard, Nature 372 (1994) 761.
[5] C.H. Kiang, J.S. Choi, T.T. Tran, A.D. Bacher, J. Phys. Chem. B 103 (1999) 7449.
[6] B.K. Pradhan, T. Kyotani, A. Tomita, J. Chem. Soc., Chem. Commun. (1999) 1317.
[7] D. Ugarate, A. Chatelain, W.A. de Heer, Science 274 (1996) 1879.
[8] J. Sloan, M.C. Novotny, S.R. Baily, G. Brown, C. Xu, V.C. Williams, S. Friedrichs, E. Flahaut, R.L. Callender, A.P.E. York, K.S. Coleman, M.L.H. Green, R.E. Dumin-Borkowski, J.L. Hutchison, Chem. Phys. Lett. 329 (2000) 61.
[9] C.C. Chen, C.C. Yeh, C.H. Liang, C.C. Lee, C.H. Chen, M.Y. Yu, H.L. Liu, L.C. Chen, Y.S. Lin, K.J. Ma, K.H. Chen, J. Phys. Chem. Solids 62 (2001) 1577.
[10] P. Chen, X. Wu, J. Lin, K.L. Tan, J. Phys. Chem. B 103 (1999) 4559.
[11] Y. Zhang, N.W. Franklin, R.J. Chen, H. Dai, Chem. Phys. Lett. 331 (2000) 35.
[12] W. Han, S. Fan, Q. Li, Y. Hu, Science 277 (1997) 1287.
[13] H. Dai, E.W. Wong, Y.Z. Lu, S. Fan, C.M. Liber, Nature 375 (1995) 769.
[14] S. Subramoney, Adv. Mater. 10 (1998) 15.
[15] Y.K. Chen, A. Chu, J. Cook, M.L.H. Green, P.J.E. Harris, R. Heesom, M. Humphries, J. Sloan, S.C. Tsang, J.F.C. Turner, J. Mater. Chem. 7 (1997) 545.
[16] H.J. Yuan, P. Xie, J. Xiang, D.P. Xu, J. Xu, S.S. Xie, S.Q. Feng, Solid State Commun. 119 (2001) 573.
[17] P.M. Ajayan, O. Stephan, Ph. Redlich, C. Colliex, Nature 375 (1995) 564.
[18] C.P. Huu, N. Keller, L. Charbonniere, R. Ziessel, M.J. Ledoux, Chem. Commun. (2000) 1871.
[19] D.J. Smith, R.M. Pisher, L.A. Freeman, J. Catal. 72 (1981) 51.

[20] P. Chen, H.B. Zhang, G.D. Lin, Q. Hong, K.R. Tsai, Carbon 35 (1997) 1495.

[21] Z.Y. Zhong, H. Chen, S. Tang, J. Ding, J. Lin, K.L. Tan, Chem. Phys. Lett. 330 (2000) 41.

[22] S. Tang, Z.Y. Zhong, Z. Xiong, L. Sun, L. Liu, J. Lin, Z. Shen, K.L. Tan, Chem. Phys. Lett. 350 (2001) 19.

[23] L.D. Mansker, Y. Jin, D.B. Bukur, A.K. Datye, Appl. Catal. A 186 (1999) 277.

[24] A. Königer, C. Hammerl, M. Zeitler, B. Rauschenbach, Phys. Rev. B 55 (1997) 8143.

[25] A. Badzian, T. Badzian, Diamond Relat. Mater. 5 (1996) 93.

[26] A. Cottrell, Chemical Bonding in Transition Metal Carbides, The University Press, Cambridge, 1995 (Chapters 1 and 2).

[27] P. Hooker, B.J. Tan, K.J. Klabunde, S. Suib, Chem. Mater. 3 (1991) 847.

[28] V.V. Chesnokov, V.I. Zaikovskii, R.A. Buyanov, J. Mol. Catal. A: Chem. 158 (2000) 267.

[29] V.P. Dymont, M.P. Samtsov, E.M. Nekrashevich, Tech. Phys. 45 (2000) 905.

[30] M. Bilaniuk, J.M. Howe, Interface Sci. 6 (1998) 317.

[31] Z.Y. Zhong, T. Prozorov, I. Felner, A. Gedanken, J. Phys. Chem. B 103 (1999) 947.

[32] R. Saito, G. Dresselhaus, M.S. Dresselhaus, Physical Properties of Carbon Nanotubes, Imperial Colleague Press, 1998 (Chapter 1).

[33] R. Gao, Z.L. Wang, S. Fan, J. Phys. Chem. B 104 (2000) 1227.

[34] X.Q. Zhao, B.X. Liu, Y. Liang, Z.Q. Hu, J. Magn. Magn. Mater. 164 (1996) 401.

[35] B. Rajesh, K.R. Thampi, J.M. Bonard, B. Viswanathan, J. Mater. Chem. 10 (2000) 1757.