JOURNAL OF MATERIALS SCIENCE **36** (2001) 4315–4320

Ultrafine magnetic metal dispersed carbons prepared from anisotropic pitch and metal acetylacetonate complexes

MASAYA KODAMA
Energy Storage Material Division, National Institute for Advanced Industrial Science and Technology, Onogawa 16-1, Tsukuba, Ibaragi 305-8569, Japan
E-mail: m.kodama@aist.go.jp

KUNIO ESUMI, HIDEMASA HONDA
Faculty of Science, Science University of Tokyo, Institute of Colloid and Interface Science, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162, Japan

Transition metal (Fe, Co or Ni) dispersed carbon composites were prepared using the mixtures of metal acetylacetonate complex as a source of metal particles and an anisotropic coal-tar pitch as a carbon matrix precursor by heat treatment at the temperatures up to 1000°C. Mixing of the metal complexes and the pitch by dissolving in quinoline permitted the notable fine dispersion of the complex in the pitch. Then the resulting mixtures were easily converted to the metal dispersed carbons by pyrolysis under an inert atmosphere. The appeared particles were Fe_3O_4/α-Fe/Fe_3C, β-Co or Ni when using the corresponding metal complex. Besides, their particle diameters were much less than 30 nm and distributed evenly throughout the carbon matrix. The magnetic properties of the metal dispersed carbons were evaluated with a vibrating sample magnetometer, and it was found that saturation magnetization and coercive force ranged from 1.03×10^{-5} to 5.65×10^{-5} Wb · m/kg and from 0.21×10^{4} to 3.06×10^{4} A/m, respectively.

1. Introduction

Metal dispersed carbons are versatile composite materials because of novel chemical properties of carbon as a support material [1–3]. Especially, many workers have been focused their attention to use them for catalysts. There are numerous methods for applying metals to carbon body, such as ion exchange [4–7], impregnation [8–12] and other methods [13–15]. The aim in these methods is how to disperse a metal (or metal source) into a carbon body. Further, the carbons containing finely dispersed ultrafine metal particles (less than 100 nm in diameter) are expected to apply for magnetic utilization or sensors depending on a kind of the metal. Recent approaches are mainly using various organometallic compounds such as metallocenes and organometallic polymers [16–26]. They are specially synthesized and used alone or together with other polymer compounds for the source of carbon matrix. These methods took advantage of an atomic level dispersion of the metal species in the precursor polymers. In some cases, finely dispersed metal in carbon certainly resulted from these concepts. However, in not a few cases, even atomic level dispersion cannot prevent the metal particles from aggregating during pyrolysis. This is because that the organic polymers have relatively low carbonization yield (sometimes less than 20%) after heat treatment. In addition, the heat treatment under a high pressure ($>$100 MPa) or with a very slow heating rate ($<$0.5°C/min) was required in most cases. This causes a difficulty in process and an increasing in the cost for preparing a large amount of the metal dispersed carbon. Another approach is to use a carbonaceous bitumen for carbon precursor. Lately, the combination of an ordinary coal-tar pitch and organometallic complexes has been reported by Yasuda and co-workers [27–29]. They widely examined a series of organometallic complexes for a metal source, and succeeded in getting some sufficient metal dispersed carbons. However no detailed data for each case was reported. Especially, presented TEM photographs were unfortunately only for limited samples. Moreover, a low pitch used as carbon precursor is not always suitable for present purpose, for instance, because of its low carbon yield.

Here, we should also note to use the precursor having a higher carbonization yield so as to prepare sufficient metal dispersed carbons. This concept is very important for preventing appeared metal particles from aggregation. On the basis of this viewpoint, an anisotropic pitch prepared from a coal-tar pitch was selected as the carbon precursor. This pitch will give more than 80 wt% of the residual carbon after carbonization up to 1000°C (higher than that of any other polymers), and, more conveniently, dissolves in quinoline completely. Besides, we chose a metal acetylacetonate complex as the metal

TABLE I Analytical values of anisotropic pitch used

Elements (wt%)				Insoluble fraction for solvent (wt%)			Softening point (°C)	Anisotropic content (%)
C	H	N	O_{diff}	Quinoline	Pyridine	Xylene		
92.2	3.5	2.6	1.7	0.0	31.5	92.5	300	100

source because of its low molecular weight (heavy ligand hydrocarbons probably being the cause of low carbon yield), ease of handling, and availability for many kinds of the coordinated metal.

The present study describes the preparation of the magnetic metal (Fe, Co or Ni) dispersed carbons by pyrolysis of the complex and pitch mixtures and the characterization of obtained samples by means of several analytical methods.

2. Experimental section

2.1. Materials

The anisotropic pitch used was prepared from a hydrogenated coal-tar pitch by heat treatment. Whereas this pitch throughout exhibits an optical anisotropic microtexture under a polarized light microscope, it is free from a quinoline insoluble fraction. The elemental analysis data and solubility in several organic liquids of this pitch are summarized in Table I. Three kinds of metal acetylacetonate complexes [M(acac)] as an additive to the pitch were used in the present study. Their coordinated metal was iron(III) cobalt(III) or nickel(II). These complexes were commercially available reagents supplied by Dojindo Laboratories Co. Ltd. and employed without further purification.

2.2. Preparation and heat treatment of complex/pitch mixtures

Ten grams of the pitch and a weighed amount of the M(acac) were dissolved together in 500×10^{-6} m^3 of quinoline at 80°C for 3 hours with stirring. Then, the quinoline was completely removed by vacuum distillation, consequently, M(acac)/pitch mixture was obtained as a residual solid. Furthermore, this mixture was pulverized to pass 200 Tyler mesh. The M(acac)/pitch mixture was heat-treated with a horizontal tube furnace at temperatures between 300 and 1000°C for 60 min in an argon atmosphere at a heating rate of 5°C/min.

2.3. Measurements

An X-ray powder diffraction (XRD) pattern of each sample was collected using a powder diffractometer equipped with a copper target X-ray tube. (Though it is widely known that the Cu K_α radiation might not be suitable for certain kind of iron compounds, we have preliminarily confirmed its feasibility in the present case.) Weight changes during heat treatment up to 1000°C were measured with a thermogravimeter (TG) under the condition of 5°C/min of heating rate and 150×10^{-6} m^3/min of a nitrogen flow. The images of obtained metal dispersed carbon samples were taken with a transmission electron microscope (TEM) operating at 200 kV accelerating voltage. And a magnetic property of the samples was evaluated using a vibrating sample magnetometer (VSM) at room temperature.

3. Results and discussion

3.1. Mixture of M(acac) and anisotropic pitch

As described in the previous section, it is expected that dispersibility of the M(acac) in starting mixture affects that of metal particle in resulting composite, therefore, to intersperse the M(acac) throughout the pitch as completely as possible is essential. From this standpoint, a dry grinding of powders, although the simplest method, was seemed to be insufficient for mixing the M(acac) and the pitch. Accordingly, the M(acac) and the pitch were blended by dissolving in quinoline. Fig. 1 shows XRD profiles of $Fe(acac)_3$ complex, the green pitch, and their mixtures (10 wt% of the complex added to the pitch) by two mixing methods mentioned above. In the case of dry mixing (grinding) of two powders (Fig. 1c) the blending was evidently insufficient, because strong diffraction peaks due to $Fe(acac)_3$ appeared over the diffraction profile of the pitch. To the contrary, uniformly dispersed $Fe(acac)_3$ in the pitch allowed to extinguish its diffraction peaks (Fig. 1d). Namely, $Fe(acac)_3$ molecules were so finely dispersed in the pitch that they

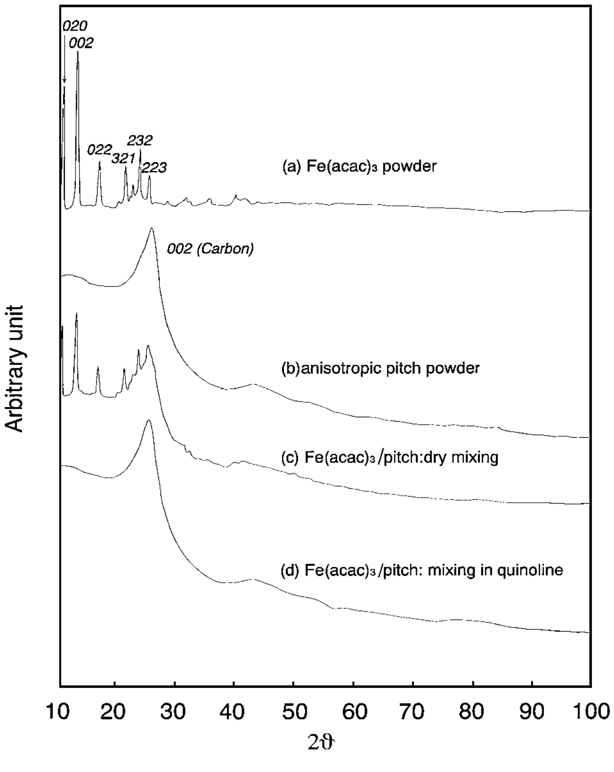


Figure 1 X-ray diffraction patterns of (a) $Fe(acac)_3$, (b) anisotropic pitch, and (c, d) their mixtures (dry grinding or mixing in quinoline). The data have been offset sequentially for comparison.

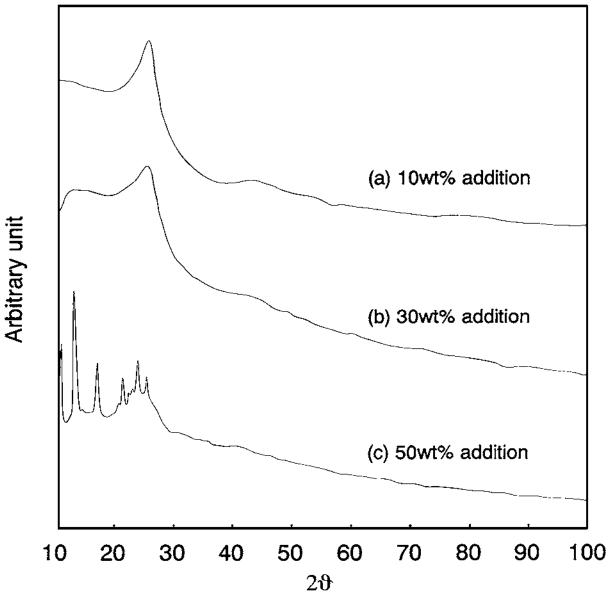


Figure 2 X-ray diffraction patterns of Fe(acac)$_3$/pitch mixtures at (a) 10 wt%, (b) 30 wt% and (c) 50 wt% of complex added. The data have been offset sequentially for comparison.

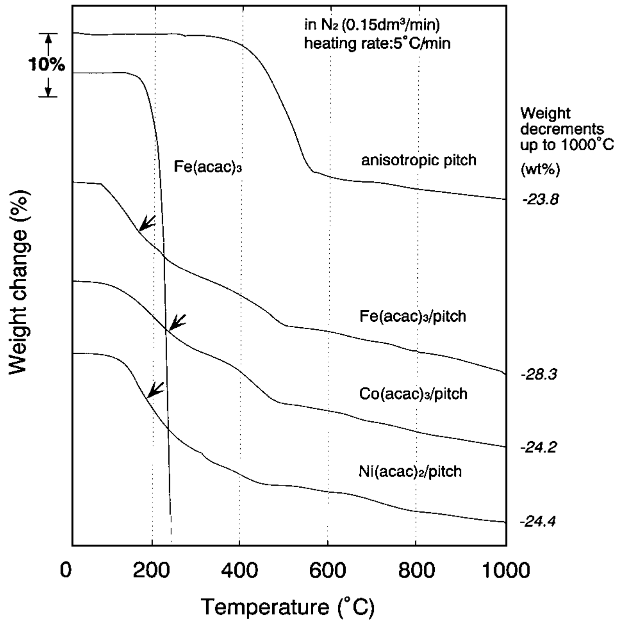


Figure 3 TG curves of the pitch and M(acac)/pitch mixtures during heat treatment up to 1000°C in N_2 atmosphere. Arrows correspond to the weight loss due to vaporization of the ligand of M(acac). The data have been offset vertically by 10 wt% for comparison.

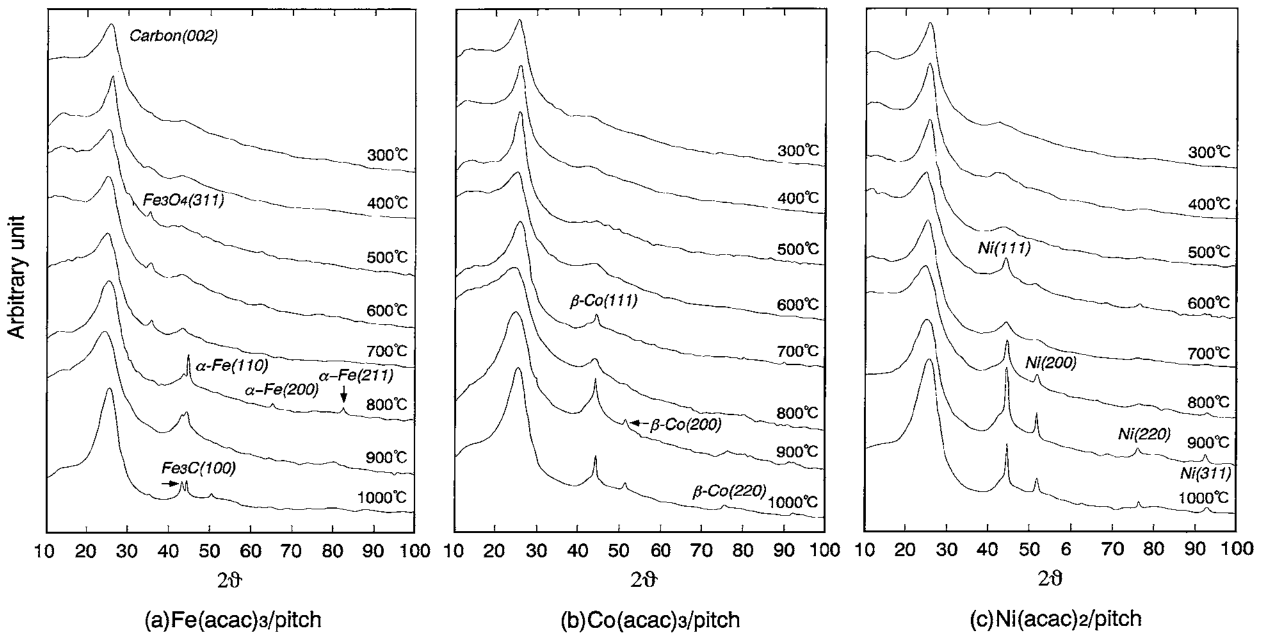
could not be detected by XRD. Next, the change in XRD profiles of the M(acac)/pitch with additive amount of the M(acac) is shown in Fig. 2. Clearly, over 30 wt% of the complex was able to add in the pitch without evident peaks on XRD by the dissolving method in quinoline. Overlapping weak broad diffraction probably due to Fe(acac)$_3$ can be seen on the carbon profile between 10 and 25° of diffraction angle in Fig. 2b. Nevertheless, the complex is still dispersed sufficiently compared with the case shown in Fig. 1c where the pitch includes only one-third amount of the complex. However, as shown in Fig. 2c, crystallization results from addition of 50 wt% of the complex, which may lead to the enlargement of metal particles dispersed in resulting carbon matrix.

3.2. Weight changes up to 1000°C

Fig. 3 shows changes in the weight of the anisotropic pitch, Fe(acac)$_3$ and M(acac)/pitch (1:10 mixture by weight) up to 1000°C in N_2 atmosphere measured using the TG (the data for Co(acac)$_3$ and Ni(acac)$_2$ were almost same as that of Fe(acac)$_3$). When the pitch was heat-treated alone, the weight change curve can be divided into three ranges. Thus, the weight scarcely changed until 350°C (range I). The weight decreased around 350°C because of commencement of carbonization reaction, and between 400 and 550°C sharply decreased on account of pyrolysis with polycondensation reactions (range II). And then, the weight gradually diminished up to 1000°C (range III). The residual weight at 1000°C was 76.2 wt%. On the other hand, in the case of three M(acac)/pitch mixtures, they showed similar TG curves. The weight began to decrease at 100–150°C in contrast to no change of the pitch under 350°C. This decrement was ascribable to the decomposition of the M(acac). However, the starting temperatures of weight decrease were lower than those of M(acac) alone. And, after losing weight corresponded to the ligand of M(acac) (they are shown by arrows in Fig. 3), the M(acac)/pitch showed further decrement up to 500°C. In addition, the marked decrement between 400 and 550°C (the range II) was no longer clearly observed, and the transition temperatures to the range 3 are lower than that in the case of using pitch alone. As the summary in Fig. 3 shows, the pyrolysis of the organic species in the M(acac)/pitch shifted to lower temperature compared with those in the sole M(acac) and pitch. This means the reactions were affected by the interaction of M(acac) and pitch. Whereas the added complexes might catalyze polycondensation reactions of aromatic hydrocarbons, the details of the carbonization stage are not clear.

3.3. XRD measurements of heat-treated samples

Fig. 4 illustrates powder XRD profiles of the M(acac)/pitch (1:10 by weight) mixtures heat-treated at temperatures for each 100°C rise between 300 and 1000°C. The every sample heat-treated at 300°C showed a XRD profile with broad (002) peak around 26° and weak (10) peak around 43°. These are typical profiles with this kind of carbonaceous anisotropic pitch. In the case of Fe(acac)$_3$/pitch (Fig. 4a), a broad peak due to Fe_3O_4 (magnetite) appeared at 400°C, then, it sharpened at 500°C and could be seen until 700°C. Over 800°C, the peak of Fe_3O_4 has disappeared and several strong peaks arose instead. These peaks can be assigned to α-Fe, which should result from reduction of the Fe_3O_4. Accompanying appearance of α-Fe, a diffraction signal from Fe_3C(100) (cementite) near the α-Fe(110) could also be seen at 800°C. With increasing heat treatment temperature (HTT) this peak grew gradually in contrast to diminishment of the α-Fe peaks. This indicates that the α-Fe can react to the carbon matrix above 800°C. In brief, the iron from pyrolized complex in the pitch has been reduced from an oxide to a carbide via metal.



(a)Fe(acac)3/pitch (b)Co(acac)3/pitch (c)Ni(acac)2/pitch

Figure 4 X-ray diffraction profiles of M(acac)/pitch mixtures heat-treated between 400°C and 1000°C at every 100°C. The data have been offset sequentially for comparison.

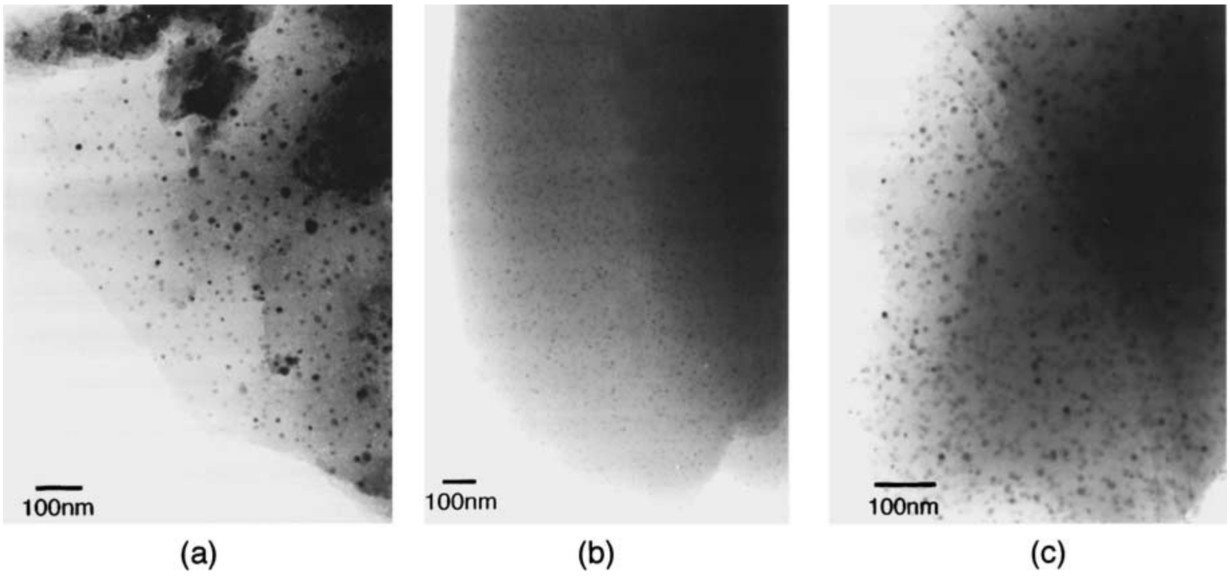


Figure 5 Transmission electron micrographs of ultrafine metal dispersed carbons. (a) Fe (900°C), (b) Co (800°C) and (c) Ni (800°C).

On the other hand, Co(acac)$_3$/pitch and Ni(acac)$_2$/pitch revealed similar XRD profile with HTT. Namely, only diffraction peaks due to corresponding metallic crystals were observed. The peaks could be detected above 700°C for Co and 600°C for Ni, then they rose and sharpened with HTT. This result suggests the augmentation of crystallinity accompanied by the growth of metal particles in the carbon.

For the Co(acac)$_3$/pitch at 400–600°C, they showed magnetizm as will be mentioned in the following section; the ferromagnetic species already appeared in the carbon in spite of no XRD peak denoting the presence of metal.

3.4. TEM observation of metal dispersed carbons

Fig. 5 shows the transmission electron micrographs of the M(acac)/pitch (1:10) mixtures heat-treated at 900, 600 and 800°C for Fe-, Co- and Ni-complex, respectively. The dispersed metals can be seen as black dots in these photographs. According to the XRD results as described earlier, these particles are α-Fe/Fe$_3$C, β-Co and Ni after undergoing the heat treatment at those temperatures. As is shown in these photographs clearly, every metal is very finely and uniformly dispersed in carbon matrix. And their particle diameters were found to be $<$25 nm for α-Fe/Fe$_3$C, $<$5 nm for β-Co and $<$15 nm for Ni. Compared with the size of metal species in the three samples, Co particles were the smallest throughout the HTT.

As far as we are aware, our result is one of the most successful cases because the metal particle sizes are much smaller than those prepared from another precursor compound. Moreover, the significance of present study is to be achieved by simple preparation method using only easily available metal complex species.

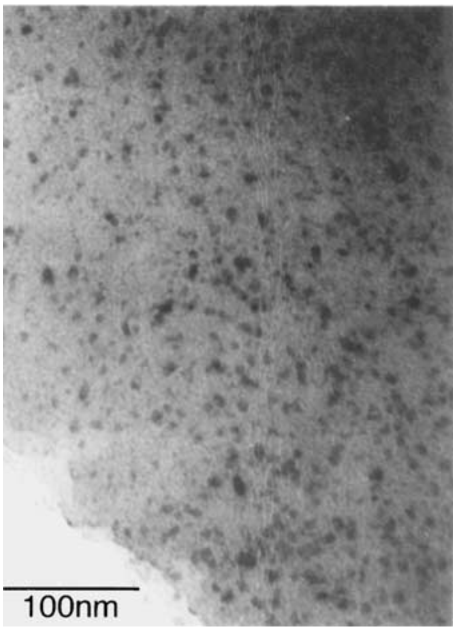


Figure 6 Transmission electron micrographs of the Fe(acac)$_3$/pitch (1:10) heat-treated at 600°C for 1 hour. The dispersed particles are mainly magnetite (Fe$_3$O$_4$).

The diameter of dispersed metals increased with the HTT as previous workers also pointed out [4, 9] and this tendency was pronounced at HTTs over 900°C. As shown in Figs 6 and 7, the diameter of dispersed Fe particles was less than 10 nm at 600°C. Clearly, they are smaller than that in Fig. 5a (at 900°C). Similarly, for Co the particle size after heat treatment at 1000°C was 10–25 nm (cf. <5 nm at 800°C). At the temperatures between 400 and 600°C for Co, where no peak from the metal species can be seen on the XRD profile, the TEM observation revealed that particles, which may be metal, already appeared in the carbonaceous matrix. On the other hand, the larger amount of M(acac) added to the pitch caused distinct enlargement of dispersed particle size. For 50 wt% addition of Fe(acac)$_3$, as shown in Fig. 8, the particle size went up to over 40 nm even at 500°C, and in this case, plenty of smaller particles also were observed in the same sample. This means the dispersion of the complex was originally heterogeneous due to much larger amount of additive.

3.5. Magnetic property of metal dispersed carbons

The samples heat-treated over 500°C (for Fe), 400°C (for Co) and 500°C (for Ni) were attracted by a magnet. These results are substantially in accordance with appearance of diffraction peaks due to ferromagnetic species on the XRD profiles. In the case of Co, the samples heat-treated between 400–600°C showed magnetism in spite of no peaks on XRD profile. The TEM observation already exhibited the presence of very small cobalt particles certainly appeared in the carbon.

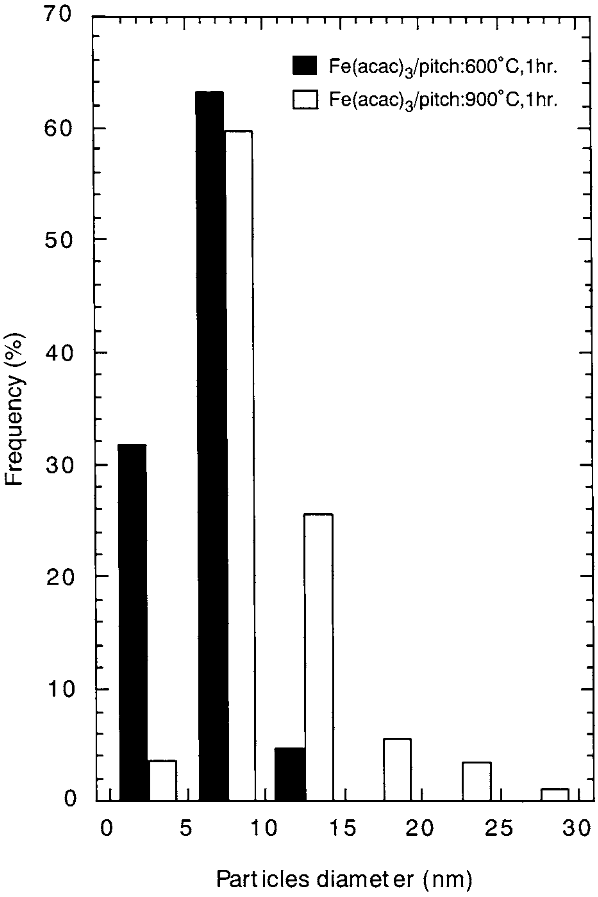


Figure 7 Particle size distribution of metal (evaluated on TEM micrographs) in heat-treated Fe(acac)$_3$/pitch mixture.

In order to evaluate the quantitative magnetic property, the samples were measured using the VSM. Obtained magnetic properties of the metal dispersed carbons heat-treated at 800°C are given in Table II. The saturation magnetization (Ms) was 1.03×10^{-5}–3.08×10^{-5} Wb · m/kg for 10 wt% of M(acac) addition. The magnification of Ms depends on the inherent value of each ferromagnetic species. Thus the Ms is proportional to the content of ferromagnetic substance in the carbon matrix. Actually, the increment of the Ms between 10 and 30 wt% of Fe(acac)$_3$ addition can be

TABLE II Magnetic properties of metal dispersed carbons heat-treated at 800°C for 1 hour

Complex	Amount of additive (wt%)	HTT (°C)	Saturation magnetization: Ms (10^{-5} Wb · m/kg)	Remanent induction:Br (10^{-5} Wb · m/kg)	Coercive force:Hc (10^4 A/m)
Fe(acac)$_3$	10	800	2.09	0.21	0.56
Fe(acac)$_3$	30	800	5.65	1.23	1.23
Co(acac)$_3$	10	800	3.08	0.94	3.06
Co(acac)$_3$	30	800	5.23	1.38	1.75
Ni(acac)$_2$	10	800	1.03	0.16	0.76
Ni(acac)$_2$	30	800	1.87	0.23	0.50

Figure 8 Transmission electron micrographs of the Fe(acac)$_3$/pitch (5:10) heat-treated at 500°C for 1 hour.

explained by this concept. The coercive force (Hc) was 0.56–3.06 × 10^4 A/m for 10 wt% of M(acac) addition. The Hc of the Co dispersed carbon was by far the highest value. Though the direct comparison of the three different metals is difficult, the high Hc value of Co-dispersed carbon could be ascribable to the small size of the Co particles. Only from the standpoint for improving Ms value, it is essential to increase the dispersed metal content in the carbon, and this is not a laborious work. However, in this case, aggregation and growth of dispersed metal particles are inevitable. This can result in lower Hc value because of multiple magnetic domains.

4. Conclusions

The M(acac)/pitch (M = Fe, Co or Ni) mixtures were easily converted into the ultrafine metal dispersed carbon composite by heat treatment at temperatures up to 1000°C. Obtained samples contained uniformly dispersed metal (partly oxide or carbide) particles having less than 30 nm in diameter. This excellent dispersibility of the metal particles was supported by the well-mixed complex/pitch and high carbon yield of the anisotropic pitch.

Acknowledgment

We express our thanks to Dr. Kazuhisa Murata of National Institute of Materials and Chemical Research for his useful discussions on magnetic measurement.

References

1. R. RADOVIC and F. RODRÍGUEZ-REINOSO, in "Chemistry and Physics of Carbon Vol. 25" (Marcel Dekker, 1998) p. 243.
2. W. AIREY, S. I. AJIBOYE, P. A. BARNES, D. R. BROWN, S. C. J. BUCKLEY, E. A. DAWSON, K. F. GADD and G. MIDGLEY, *Catal. Today* **7** (1990) 179.
3. H. MARSH, F. DACHILLE, J. MELVIN and P. L. WALKER JR, *Carbon* **9** (1971) 159.
4. D. RICHARD and P. GALLEZOT, in "Preparation of Catalysts IV" (Elsevier, Amsterdam, 1987) p. 71.
5. A. GIROIR-FENDLER, D. RICHARD and P. GALLEZOT, in "Heterogeneous Catalysis and Fine Chemicals" (Elsevier, Amsterdam, 1988) p. 171.
6. M. BESSON, L. BULLIVANT, N. NOCOLAUS-DECHAMP and P. GALLEZOT, in "Heterogeneous Catalysis and Fine Chemicals III" (Elsevier, Amsterdam, 1933) p. 115.
7. P. GALLEZOT, M. BESSON and F. FACHE, in "Catalysis of Organic Reactions" (Marcel Dekker, New York, 1995) p. 331.
8. P. FOUILLOUX, in "Heterogeneous Catalysis and Fine Chemicals" (Elsevier, Amsterdam, 1988) p. 123.
9. S. M. A. M. BOUWENS, D. C. KONINGSBERGER, V. H. J. DE BEER and R. PRINS, in "Characterization and Catalyst Development: An Interactive Approach" (American Chemical Society, Washington, D.C., 1989) p. 319.
10. M. W. J. CRAJÉ, E. GERKEMA, V. H. J. DE BEER and A. M. VAN DER KRAAN, in "Advances in Hydrotreating Catalysts" (Elsevier, Amsterdam, 1989) p. 165.
11. F. M. BAUTISTA, J. M. CAMPELO, A. GARCIA, R. GUARDEÑO, D. LUNA and J. M. MARINAS, in "Heterogeneous Catalysis and Fine Chemicals II" (Elsevier, Amsterdam, 1991) p. 269.
12. S. GALVAGNO, C. MILONE, G. NERI, A. DONATO and R. PIETROPAOLO, in "Heterogeneous Catalysis and Fine Chemicals III" (Elsevier, Amsterdam, 1993) p. 163.
13. K. DELLER and B. DESPEYROUX, in "Catalysis of Organic Reactions" (Marcel Dekker, New York, 1992) p. 261.
14. R. BURMEISTER, B. DESPEYROUX, K. DELLER, K. SEIBOLD and P. ALBERS, in "Heterogeneous Catalysis and Fine Chemicals III" (Elsevier, Amsterdam, 1993) p. 361.
15. Y. NITTA, T. KATO and T. IMANAKA, in "Heterogeneous Catalysis and Fine Chemicals III" (Elsevier, Amsterdam, 1993) p. 83.
16. S. HIRANO *et al.*, *J. Mater. Sci.* **18** (1983) 2811; **21** (1986) 2571; **22** (1987) 985; **24** (1989) 2071; **24** (1989) 2115.
17. S. HIRANO, T. YOGO, H. SUZUKI and S. NAKA, *ibid.* **18** (1983) 2811.
18. T. YOGO, H. SUZUKI, S. NAKA and S. HIRANO, *ibid.* **21** (1986) 2571.
19. S. HIRANO, T. YOGO and S. NAKA, *ibid.* **22** (1987) 985.
20. T. YOGO, S. NAKA and S. HIRANO, *ibid.* **24** (1989) 2071.
21. *Idem.*, *ibid.* **24** (1989) 2115.
22. H. YOKOI, S. KAWATA and M. IWAIZUMI, *J. Am. Chem. Soc.* **108** (1986) 3358.
23. S. I. AJIBOYE and D. R. BROWN, *J. Chem. Soc. Faraday Trans.* **86** (1990) 65.
24. S. HIRANO, T. YOGO, N. NOGAMI and S. NAKA, *J. Mater. Sci.* **21** (1986) 225.
25. T. YOGO, E. TAMURA, S. NAKA and S. HIRANO, *ibid.* **21** (1986) 941.
26. Y. OHTSUKA, T. WATANABE, Y. NISHIYAMA, M. MATSUDA and H. YOKOI, *ibid.* **29** (1994) 877.
27. H. YASUDA, A. HIWARA, A. NAKAMURA and H. SAKAI, *J. Inorg. Organomet. Polym.* **1** (1991) 135.
28. *Idem.*, *ibid.* **1** (1991) 239.
29. S. MIYANAGA, H. YASUDA, A. HIWARA and A. NAKAMURA, *J . Macromol. Sci. Chem. A* **27** (1990) 1347.

Received 18 August 1998
and accepted 19 April 2001