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Communication

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## **New Carbon Composites Containing Ultrafine Fe, Co, or Ni Particles. 1. Facile Synthesis by Pyrolysis of Organometallic Polymers**

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Uniformly dispersed, air-stable carbon composites containing ultrafine  $\alpha$ -Fe, Co, or Ni particles were obtained by a careful two-step thermal degradation of a copolymer of acrylonitrile (AN) and 2,4-hexadienyl-[tri(carbonyl)iron] acrylate. Carbonization yields were 45–55% and metal particle size ranged from 80 to 120 nm. Analogous degradation of the acrylonitrile copolymer with  $\text{CoCl}_2(\text{AN})_2$ ,  $\text{CoCl}_2(4\text{-vinylpyridine})_2$ , or Ni(*bis*-styrene carboxylate) gave similar composites containing  $\beta$ -Co (18 nm),  $\beta$ -Co (55 nm), or cubic Ni (52 nm) particles, respectively, with lower carbonization yields. Other salient features noted for the metal-containing composites are progressive graphitization promoted by catalysis of nascent metal species at low temperature, microporous structures with surface areas of 75 and 55  $\text{m}^2 \text{g}^{-1}$  for Co and Ni composites, respectively, high electrical conductivities ( $10\text{--}10^2 \text{ S cm}^{-1}$ ), ferromagnetism, and catalysis in the decomposition of  $\text{H}_2\text{O}_2$ .

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**KEY WORDS:** Carbon composites; inorganic copolymers;  $\alpha$ -iron particles;  $\alpha$ -iron-carbon composites;  $\beta$ -cobalt particles;  $\beta$ -cobalt-carbon composites; nickel particles; nickel-carbon composites; ultrafine metal particles; pyrolysis of metal-containing polymers; metal-carbon composites; electrical conductivities; catalyst; organometallic polymers.

Carbon composites containing ultrafine metal particles in carbon matrices may function as potential new catalysts, electric and magnetic devices, and

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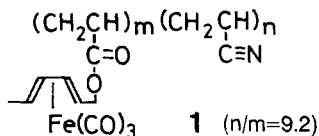
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adsorbents. All attempts to create iron metal–carbon composites by pyrolysis methods using poly(furfural/acetylferrocene) [1, 2], poly(vinyl ferrocene/divinyl benzene) [3], or polymer blends of inorganic compounds [4, 5] have given us unsatisfactory results, since the resulting products are either a pyrophoric mixture or simply iron carbide. Pyrolysis of conventional molecular organometallic complexes is also useless for the present purpose because it causes the formation of a complicated pyrophoric mixture or a thin metal film in a low yield [6]. Although pyrolysis of a mixture of furfuryl alcohol with insoluble  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  or with 1,1'-ferrocene dicarboric acid and  $\text{HNO}_3$  is reported to produce a glassy carbon containing  $\alpha$ -Fe particles, details are still unknown [7].<sup>5</sup> We wish to report herein a novel, convenient method for the synthesis of highly air-stable carbon composites containing ultrafine Fe, Co, or Ni particles of uniform diameter by careful degradation of a series of metal-containing polymers.

Heat treatment of a copolymer of acrylonitrile (AN) with 2,4-hexadienyl-[tri(carbonyl)iron] acrylate (HATI) [8]<sup>6</sup> (**1**) (Scheme I)



Scheme I

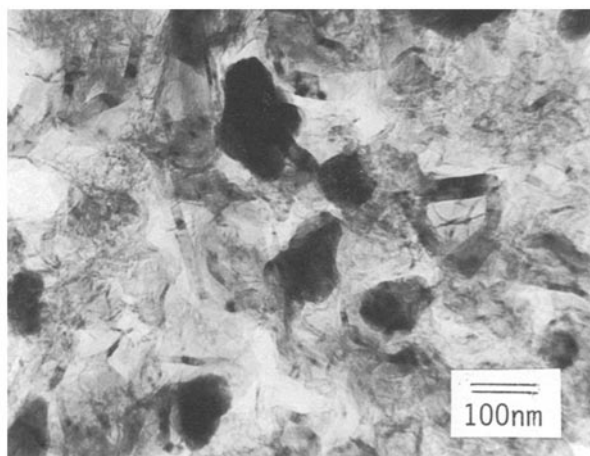
(monomer unit ratio in the polymer, 9.2:1) at 1100°C was found to provide air-stable ultrafine particles of crystalline  $\alpha$ -Fe (diameter, 80–120 nm) dispersed uniformly in the carbon matrix as confirmed by XRD [9],<sup>7</sup> Mössbauer [10],<sup>8</sup> and transmission electron micrographic (TEM) analyses (Fig. 1). Thermal treatment of the samples was conducted in a Kanthal combustion tube (bore, 6 cm; length, 100 cm) under an Ar stream (120 ml/min) by raising the temperature gradually to 350°C at a rate of 0.3°C/min and then rapidly at a rate of 1.1–1.5°C/min to 1100°C followed by a rapid cooling to 25°C. Such a two-step thermal treatment promises uniform dispersion of the resulting  $\alpha$ -Fe particles in a carbon phase. The use of metal–polymer complexes with a poly(acrylonitrile) (PAN) skeleton gave maximum carbonization yields (45–55 w% of the precursor). Thus, a copolymer of AN with vinyl ferrocene (9:1) also serves

<sup>5</sup> The exact constitution of the Fe component and carbon phase, size distribution, homogeneity of the composite, air stability, and carbonization yield are unclear.

<sup>6</sup> Copolymerization of AN with HATI (7:1) was carried out in toluene at 75°C for 24 h using AIBN (1%) as an initiator. For preparation of HATI, see Ref. 8.

<sup>7</sup> Resulting XRD patterns of metallic species were analyzed with reference to the data listed in Ref. 9.

<sup>8</sup> Analysis is based on the Mössbauer spectral data listed in Ref. 10.



**Fig. 1.** TEM profile of the Fe/C composite synthesized from poly(AN/HATI) (9.2:1) upon heat treatment at 1100°C.

as a good precursor leading to an  $\alpha$ -Fe/C composite. (C, 84.9; N, 0.3; Fe, 14.8; H and O, <0.1%; size of Fe particles, 80–120 nm; carbonization yield, 54%; Fe remaining in the composite, 56%.) In contrast, the homopolymer of HATI, in addition to its copolymers (monomer unit ratio in the polymer, ca. 1:9) with styrene, 1,4-divinylbenzene, and methyl methacrylate, all gave very low carbonization yields (5–10%) (66–81% of the products are  $\alpha$ -Fe). Most striking here is the exceedingly high stability of the resulting Fe/C composite (derived from **1**) under aerobic conditions. No oxidation of  $\alpha$ -Fe occurred on exposure to air for 1 month as revealed by Mössbauer studies. This is due to encapsulation of the metal particles by the surrounding carbon. One is reminded that activated carbons mixed or coated with ultrafine Fe particles (diameter, <2  $\mu$ m) are generally inflammable in air. No appreciable changes in size and shape of the particles as a function of metal content in the precursor polymers were noted, while the identity of the particles varied critically depending on the treatment temperatures. At 800–950°C, the poly(AN/HATI) (9.2:1) (**1**) produces only pure Fe<sub>3</sub>C particles, and during the heat treatment at 1000°C, the Fe<sub>3</sub>C is converted gradually to  $\alpha$ -Fe (21% of Fe<sub>3</sub>C remained after holding for 1 h). Finally, the Fe<sub>3</sub>C is well reduced to  $\alpha$ -Fe particles by heat treatment at 1100–1200°C as a result of the reducing power of the surrounding carbon as judged from Mössbauer spectroscopic studies (Fig. 2). Each particle is well separated from the others by the carbon phase as confirmed by EDX analysis. The present Fe/C composites prepared at 1000°C (metal content, 1–5%) are microporous and their BET specific surfaces are anomalously large (120–180 m<sup>2</sup>/g). The application of the present method

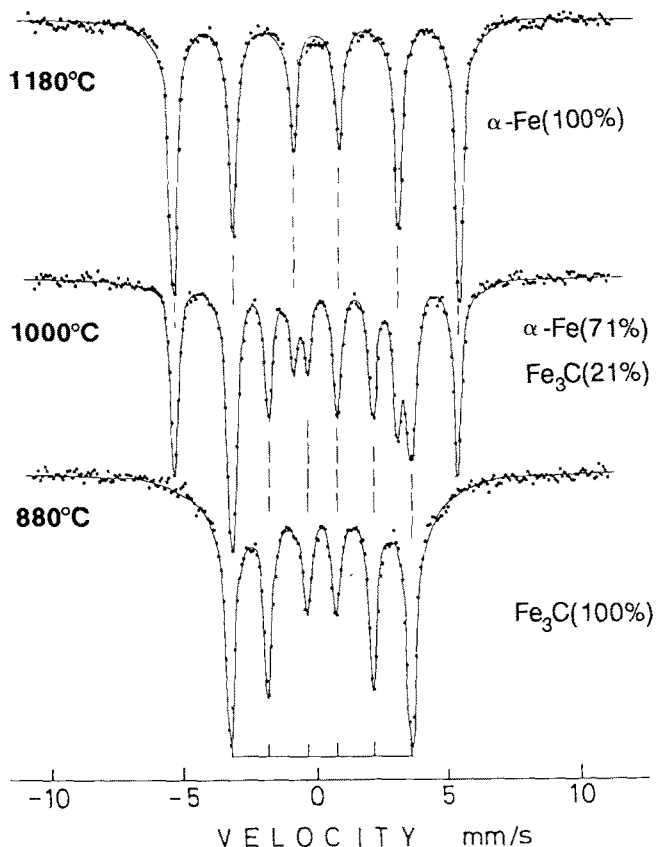
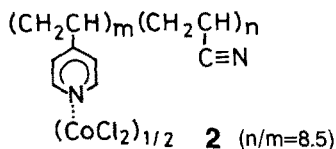


Fig. 2. Mössbauer spectral pattern for the Fe/C composites derived from poly(AN/HATI) (9.2:1) at various temperatures.

to the AN copolymers (ca. 9:1) with  $\text{CoCl}_2(\text{AN})_2$ ,  $\text{CoCl}_2(4\text{-vinyl pyridine})_2$ , and Ni-bis(styrene carboxylate)  $[\text{Ni}(\text{CH}_2=\text{CHC}_6\text{H}_4\text{COO})_2]$  also gave a vital route to similar composites containing pure  $\beta\text{-Co}$  (cubic) or nickel (cubic) particles. For example, pyrolysis of poly[AN/CoCl<sub>2</sub>(4-vinyl pyridine)<sub>2</sub>] (8.5:1) (2)<sup>9</sup> (Scheme II) at 1000°C for 1 day produced



Scheme II

<sup>9</sup> Prepared by radical polymerization of AN with  $\text{CoCl}_2(4\text{-vinyl pyridine})_2$  (7:1) in toluene at 75°C for 24 h. Yield of the resulting blue-colored polymer is 82%.

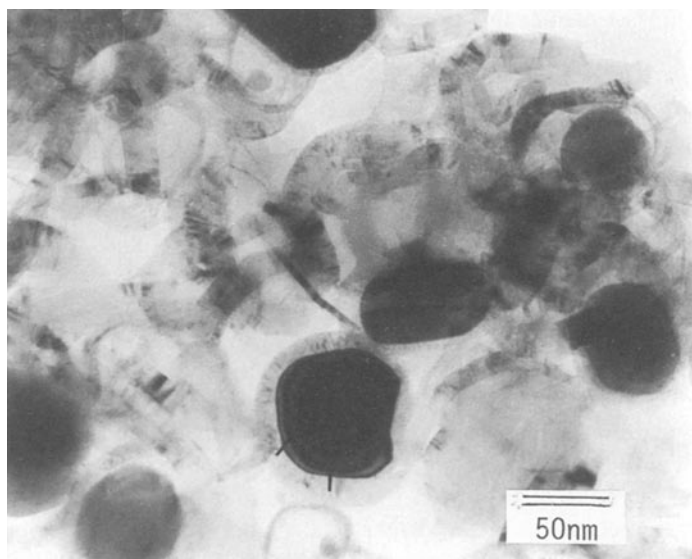
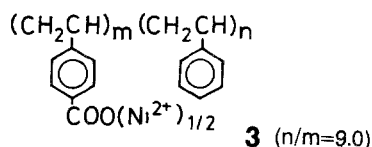


Fig. 3. TEM profile of Ni/C composite synthesized upon pyrolysis of poly[AN/(CH<sub>2</sub>=CHC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)<sub>2</sub>Ni] (9:1) at 1000°C.

an air-stable composite (C, 79.8; Co, 19.2%) containing ultrafine particles of pure  $\beta$ -Co of 18-nm (av) diameter, which is much smaller in size than the corresponding Fe particles, whereas the pyrolysis of a related copolymer, poly[styrene/CoCl<sub>2</sub>(4-vinyl pyridine)<sub>2</sub>], affords a composite containing larger particles (av 55 nm) consisting of a 3:2 mixture of  $\beta$ - and  $\alpha$ -Co, with a lower carbonization yield (12%). Pyrolysis of poly[styrene/(CH<sub>2</sub>=CHC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)<sub>2</sub>Ni]<sup>10</sup> (9:1) (**3**) (Scheme III) also



Scheme III

yielded an air-stable composite (C, 74.2; Ni, 25.1%) containing pure Ni particles [diameter, 52 nm (av); see Fig. 3], although the yield is rather

<sup>10</sup> Prepared by mixing a THF/water solution of partially hydrocarboxylated (10%) polystyrene with a EtOH solution of NiCl<sub>2</sub>·H<sub>2</sub>O (0.11 equimol), which gave precipitation of a pale green polymer in a 98% yield.

low (16–22%). Thus, the use of PAN systems, which degrade without melting, generally leads to finer and well-dispersed metal particles.

Remarkable features observed commonly in the present products obtained from **1** to **3** (treated at 1000°C) are the following. (i) Progressive graphitization is promoted by the catalysis of nascent metal species even at 1000°C, a much lower temperature than that required for graphitization of the conventional metal-free PAN (>2000°C). The extents of graphitization estimated from Warren's  $p_1$  values [11] are 80, 74, and 70% for the Fe-, Co-, and Ni-carbon composites, respectively. Such a catalytic effect compares very closely with that reported for the gas-phase carbon whisker formation from olefins and benzene catalyzed by these metals [12, 13]. (ii) The composites are air-stable and microporous. The effective surface areas of Co and Ni composites (75 and 55 m<sup>2</sup>/g, respectively) again exceed that of carbons derived from metal-free PAN (2–14 m<sup>2</sup>/g). (iii) High electrical conductivities (10–10<sup>2</sup> S cm<sup>-1</sup>) exist in these composites (metal content, <5%) as a result of enhanced graphitization of the carbon component, not by the direct effect of the dispersed metal as revealed by temperature-dependent conductivity measurement (i.e., the change in conductivity is <3 S cm<sup>-1</sup> between -40 and 100°C).<sup>11</sup> (iv) The composites are all ferromagnetic. The coercive forces for the composites derived from **1**, **2**, and **3** are 111, 402, and 343 Oe, respectively. Thus, these composites may have potential utility as a new absorbent for electromagnetic waves and new types of magnetic devices with a high conductivity. (v) A unique catalytic effect of the metals was observed in the cracking of 5–30% aq. H<sub>2</sub>O<sub>2</sub> to evolve oxygen. The activities for Fe, Co, and Ni composites are 284, 186, and 5 mol/g-M·h, respectively, whereas commercially available Fe particles (diameter, ca. 0.1 mm) show practically no activity. Further studies of new applications of these materials are now under way.

## ACKNOWLEDGMENT

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<sup>11</sup> Conductivity was measured by the conventional four-terminal DC method in vacuum using samples compressed into circular pellets of diameter 10 mm and thickness ca. 0.3 mm under 3900 Kg/cm<sup>2</sup>. The value was constant irrespective of the metal content (1–15%) in the composites.

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