

# Synthesis and properties of carbons dispersed with Fe-Co alloy by pressure pyrolysis of organoiron-organocobalt copolymer

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Carbons dispersed with Fe-Co alloy were synthesized by the pressure pyrolysis of vinylferrocene-phenylethynylcobaltocene-divinylbenzene copolymer at temperatures below 700°C and at 125 MPa. As-prepared carbon synthesized at 550°C contained finely dispersed metallic particles of less than 10 nm diameter with low crystallinity, which crystallized to form Fe-Co alloy particles with a higher crystallinity by subsequent heat treatment at 800°C. Larger particles of the alloy of more than 50 nm diameter were dispersed in the carbon matrix synthesized at 700°C. Thermomagnetization measurement of the as-prepared carbon synthesized from divinylbenzene-2.1 mol % vinylferrocene-4.8 mol % phenylethynylcobaltocene copolymer at 550°C and 125 MPa confirmed that iron formed an alloy with cobalt in the carbon matrix. Fine, superparamagnetic metallic particles in the as-prepared carbon aggregated and crystallized by the heat treatment during the thermomagnetic measurement to increase the magnetization of the alloy-dispersed carbon. The saturation magnetization and the coercive force of alloy-dispersed carbon increased from 128 to 187 e.m.u. g<sup>-1</sup> and from a few to 50 Oe, respectively, on increasing the pyrolysis temperature of the starting copolymer from 550 to 700°C. The saturation magnetization of alloy-dispersed carbon from divinylbenzene containing iron and cobalt with a ratio of 5:2 was higher than that from divinylbenzene including those with a ratio of 2:5. The carbon with finely dispersed Fe-Co alloy showed a high saturation magnetization of 213 e.m.u. g<sup>-1</sup> and a coercive force of 230 Oe, and the magnetization persisted above 800°C.

## 1. Introduction

The character of carbons depends on the nature of the carbon-carbon bonds of the original organic compounds and on the pyrolysis conditions such as temperature and pressure [1-9].

Carbons containing finely dispersed metallic particles can be synthesized in high yields by the pressure pyrolysis of organometallic polymers. Marsh *et al.* [2] reported the synthesis of anisotropic carbon spherulites by carbonization of a mixture of anthracene and ferrocene under pressure. Hirano *et al.* [3] demonstrated the synthesis of carbon spherulites by pressure pyrolysis of divinylbenzene copolymerized with vinylferrocene to give a fine dispersion of metal particles. Hirano *et al.* [10] synthesized carbons dispersed with iron particles from cementite-dispersed carbon obtained by the pressure pyrolysis of divinylbenzene-vinylferrocene.

The stabilities of the metal-carbon and carbon-carbon bonds of an organometallic polymer influence the properties of the metal particles in the resultant carbons. The morphology of the carbon is affected by the concentration of metals in the starting polymer as well as by the pyrolysis conditions.

The present paper concerns the synthesis and

properties of carbons dispersed with Fe-Co alloy particles by the pressure pyrolysis of organoiron-organocobalt copolymers. Dispersion of Fe-Co alloy in the carbon matrix was attempted in order to increase the saturation magnetization of metal-dispersed carbon, since Fe-Co alloy has the highest value of saturation magnetization among transition metal alloys [11]. The resulting carbon with a metallic dispersoid was characterized by X-ray diffraction analysis and thermomagnetic measurements. The saturation magnetization and coercive force of alloy-dispersed carbon were measured in order to evaluate the properties of the dispersed metallic particles.

## 2. Experimental procedures

Vinylferrocene (VF) was prepared according to Arimoto and Haven [12]. Phenylethynylcobaltocene (cyclopentadienyl (1-*exo*-phenylethynylcyclopentadiene) cobalt (I), PECo) was prepared as described by Kojima *et al.* [13]. Commercially available divinylbenzene (a mixture of 55% *m*- and *p*-divinylbenzene and 45% ethylbenzene) was employed as the organic copolymer for the carbon matrix.

Pressure pyrolyses were carried out in a hydrothermal apparatus of the cold-seal type. The required

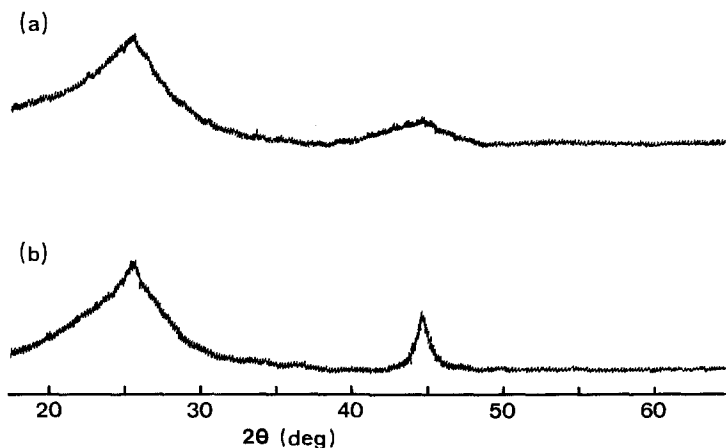


Figure 1 X-ray diffraction profiles (CuK $\alpha$  radiation) of Fe-Co-dispersed carbons. (a) As-prepared Fe-Co-dispersed carbon formed by pyrolysis of DVB-6.5 mol % VF-3.0 mol % PECo copolymer at 550°C and 125 MPa. (b) After heat treatment of (a) at 800°C for 6 h.

amounts of vinylferrocene and phenylethynylcobaltocene were dissolved in divinylbenzene (DVB) under nitrogen. The solution was sealed in a thin-walled gold capsule of 3.0 or 5.0 mm diameter and 50 mm length [4, 5].

The solutions of divinylbenzene-vinylferrocene-phenylethynylcobaltocene were polymerized at 300°C for 2 h at 100 MPa pressure and then pyrolysed at temperatures between 550 and 700°C for 3 h under 125 MPa pressure. The temperature was raised at 10°C min<sup>-1</sup> at a constant pressure of 125 MPa. The pressure was kept isobaric by releasing water as a pressure-transporting medium during heating. The pressure was measured with a calibrated Heise gauge and the temperature was controlled with a calibrated sheathed thermocouple set inside the pressure vessel. The sample was quenched after an experimental run.

The yield of carbon was as high as about 80%. The crystalline states of the metal-dispersed carbons were characterized by X-ray diffraction analysis. Prior to the subsequent heat treatment, the as-prepared specimen was evacuated at 250°C for several hours and then sealed in a quartz capsule under vacuum. The lattice constant of an alloy was determined from the 110 diffraction line referred to an internal standard of silicon. The morphology and microstructure of synthesized carbon were analysed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The synthesized specimen was desorbed and sealed into a quartz capsule and the thermomagnetization curve was then measured with a magnetic balance from room temperature to 850°C. The saturation magnetization and the coercive force of metal-dispersed carbon were evaluated using a vibrating sample magnetometer (VSM) at room temperature.

### 3. Results and discussion

#### 3.1. Synthesis of carbon dispersed with Fe-Co alloy

##### 3.1.1. X-ray diffraction studies

Carbon with the morphology of coalescing polyhedra [10] was formed from DVB-6.5 mol % VF-3.0 mol % PECo (Fe-32 at % Co) at 550°C and 125 MPa for 3 h. The X-ray diffraction profile of the product (Fig. 1a) was composed of two broad diffraction lines at  $2\theta = 25.5$  and  $44.8^\circ$  (CuK $\alpha$ ). The former is attributed to the 002 diffraction line of turbostratic

carbon and the latter to metal particles with a low crystallinity dispersed in the carbon matrix, since the 110 diffraction line of a body-centered cubic Fe-Co alloy appears between  $2\theta = 44.80$  and  $45.24^\circ$ , depending on the composition [14].

After heat treatment of the as-prepared specimen at 800°C for 6 h, the X-ray diffraction profile showed sharp diffraction at  $2\theta = 44.8^\circ$  due to an increase of crystallinity of the metallic particles (Fig. 1b).

The lattice constants of alloys dispersed in the carbon were measured after the heat treatment. When the molar proportion of PECo relative to VF in the starting copolymers increased from 31.3 to 48.6%, the lattice constant of the Fe-Co alloy decreased from 286.2 to  $285.5 \pm 0.2$  pm. This fact means that iron and cobalt in the carbon matrix formed an alloy. A similar decrease of lattice constant in the Fe-Co alloy itself has been reported as the concentration of cobalt increases from 30.3 to 48.6 at % [14].

#### 3.1.2. Microstructure of alloy-dispersed carbon

Fig. 2a represents the microstructure of carbon formed from the copolymer DVB-6.5 mol % VF-3.0 mol % PECo at 550°C and 125 MPa for 3 h. The carbon contained uniformly black particles less than 10 nm in size. On the other hand, metallic particles of diameter larger than 50 nm were dispersed in the carbon formed from a copolymer with a similar mixture ratio which was pyrolysed at the higher temperature of 700°C (Fig. 2b).

Fig. 2c shows the microstructure of the specimen shown in Fig. 2a after heat treatment at 800°C for 6 h. The alloy particles grew from 10 nm to 15 nm diameter and 140 nm length by diffusion in the carbon matrix.

### 3.2. Magnetic properties of Fe-Co-dispersed carbon

#### 3.2.1. Thermomagnetic behaviour

Figs. 3a, b and c illustrate features of the thermomagnetization curves of alloy-dispersed carbon synthesized from DVB-VF-PECo copolymers of different composition by pyrolysis at 550°C and 125 MPa for 3 h. The molar ratio of VF to PECo in DVB was 8.6/1.0 (Fe-10 at % Co), 6.5/3.0 (Fe-32 at % Co) and 2.1/4.8 (Fe-70 at % Co) for Figs. 3a, b and c, respectively.

Figs. 3a and b show similar thermomagnetic

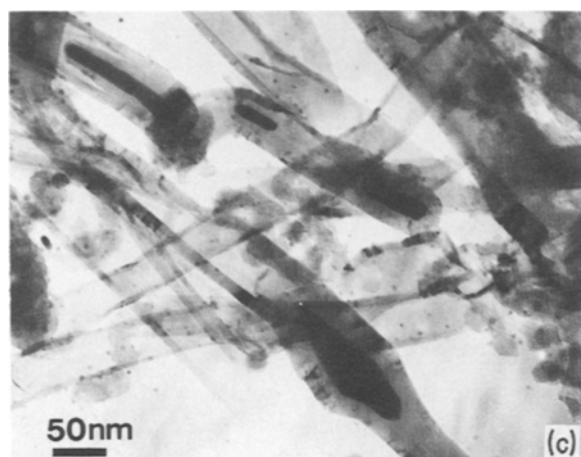
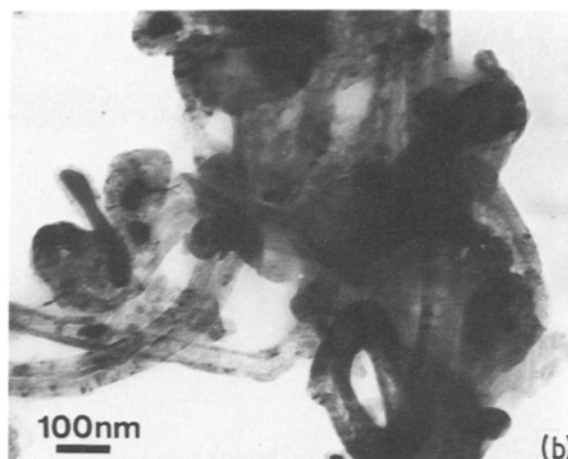
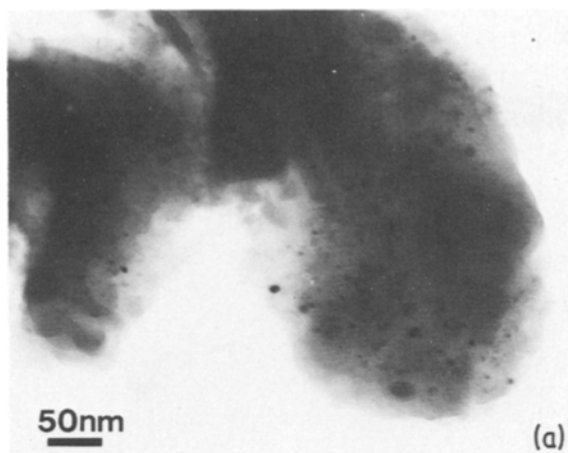


Figure 2 Microstructures of carbon dispersed with black alloy particles. (a) Carbon prepared from DVB-6.5 mol % VF-3.0 mol % PECo copolymer by pyrolysis at 550°C and 125 MPa. (b) Carbon formed from DVB-7.0 mol % VF-2.5 mol % PECo copolymer by pyrolysis at 700°C and 125 MPa. (c) Carbons containing column-shaped alloy particles synthesized by heat treatment of (a) at 800°C for 6 h.

behaviour in the first heating. However, the curves were markedly different from those of cementite- and iron-dispersed carbons [10]. The magnetization of alloy-dispersed carbons decreased with increase in temperature. The Curie point at 210°C shows the coexistence of a small amount of cementite in the specimen. The slight increase of magnetization at about 500°C is due to the formation of iron by the thermal decomposition of cementite.

The presence of the Curie point of cementite on cooling in Fig. 3a showed a different behaviour from the first cooling curve in Fig. 3b, which did not show any Curie point corresponding to cementite. Cementite was formed reversibly from active  $\alpha$ -iron and excess carbon as shown in Fig. 3a, while  $\alpha$ -iron generated during the first heating alloyed readily with cobalt as shown in Fig. 3b. When the starting copolymer contained an excess of cobalt over iron (Fe-70 at % Co), the metal-dispersed carbon did not contain any cementite even on the first heating (Fig. 3c). The amount of cobalt should therefore be adjusted to be in excess over iron in the starting polymer, in order to suppress the formation of cementite in as-prepared carbons.

No formation of cementite or free iron could be observed in the carbon specimens, and the magnetization persisted even at 820°C on the second heating as shown in Fig. 3b. This fact supports the idea that the dispersoid in the carbons is an Fe-Co alloy with a higher regularity of alloy lattice than existed before the thermomagnetic measurement.

Metal particles in the as-prepared specimen are composed of ferromagnetic and superparamagnetic Fe-Co alloy with a small amount of cementite particles, even when a large excess of iron over cobalt is contained in the starting polymer. The growth and crystallization of superparamagnetic particles proceeds during the first heating during thermomagnetic measurement to increase the magnetization of the specimen.

### 3.2.2. Saturation magnetization and coercive force

The saturation magnetization ( $\sigma_s$ ) of Fe-Co-dispersed carbon was correlated with the pyrolysis temperature of DVB-5.0 mol % VF-2.0 mol % PECo (Fe-29 at % Co) and DVB-2.0 mol % VF-5.0 mol % PECo (Fe-71 at % Co) in Fig. 4. The dashed lines in Fig. 4 give the values of  $\sigma_s$  for Fe-Co alloys with compositions corresponding to those of the starting polymers [15]. The  $\sigma_s$  of the specimen was converted to the value per gram of metals.

The  $\sigma_s$  of the alloy-dispersed carbon (Fe-29 at % Co) increased from 128 to 187 e.m.u.  $g^{-1}$  with an increase of the pyrolysis temperature from 550 to 700°C. The  $\sigma_s$  of Fe-Co-dispersed carbon synthesized at 700°C shows about 75% of the theoretical value calculated on the basis of the pure alloy. The copolymer containing a higher concentration of iron (Fe-29 at % Co) gave an alloy-dispersed carbon with a higher  $\sigma_s$  than that from the copolymer containing a higher concentration of cobalt (Fe-71 at % Co), which is in good agreement with the Fe-Co alloy showing a maximum in  $\sigma_s$  at a composition of Fe-30 at % Co [11].

Fig. 5 summarizes the coercive force ( $H_c$ ) of alloy-dispersed carbon synthesized from DVB-2.0 mol % VF-2.0 mol % PECo copolymer and DVB-5.0 mol % VF-2.0 mol % PECo copolymer at various temperatures between 550 and 700°C at 125 MPa. The  $H_c$  of Fe-Co-dispersed carbon increased with increasing

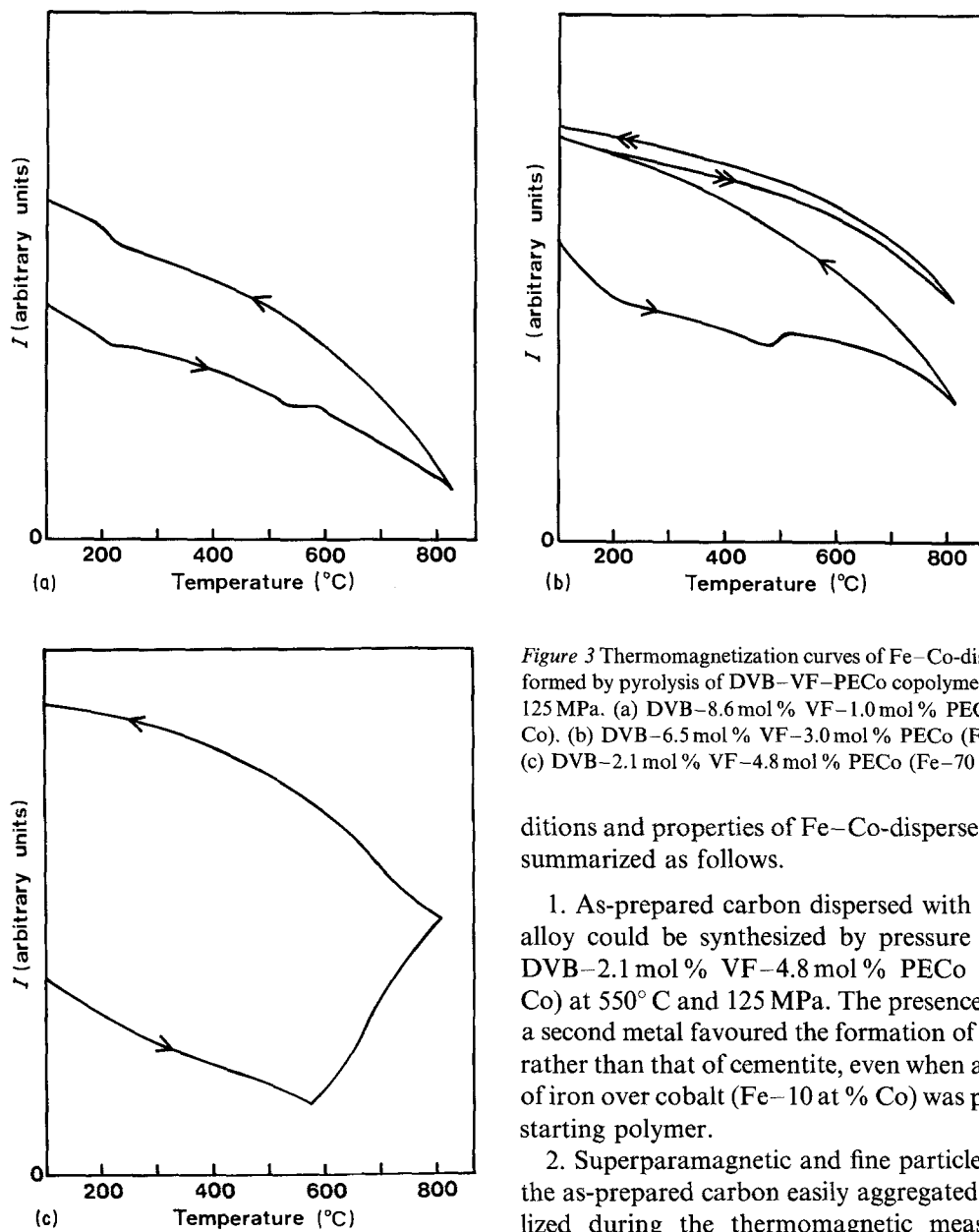


Figure 3 Thermomagnetization curves of Fe-Co-dispersed carbons formed by pyrolysis of DVB-VF-PECo copolymers at 550°C and 125 MPa. (a) DVB-8.6 mol % VF-1.0 mol % PECo (Fe-10 at % Co). (b) DVB-6.5 mol % VF-3.0 mol % PECo (Fe-32 at % Co). (c) DVB-2.1 mol % VF-4.8 mol % PECo (Fe-70 at % Co).

ditions and properties of Fe-Co-dispersed carbon are summarized as follows.

1. As-prepared carbon dispersed with only Fe-Co alloy could be synthesized by pressure pyrolysis of DVB-2.1 mol % VF-4.8 mol % PECo (Fe-70 at % Co) at 550°C and 125 MPa. The presence of cobalt as a second metal favoured the formation of Fe-Co alloy rather than that of cementite, even when a large excess of iron over cobalt (Fe-10 at % Co) was present in the starting polymer.

2. Superparamagnetic and fine particles of alloy in the as-prepared carbon easily aggregated and crystallized during the thermomagnetic measurement to

pyrolysis temperature, which led to an increase in the size of metallic particles in the carbon as shown in Fig. 2. Since metallic particles of less than 10 nm were dispersed in the carbon synthesized at 550°C (Fig. 2a), the superparamagnetic effect is responsible for the low  $H_c$  of the specimen.

When the Fe-Co-dispersed carbon synthesized from DVB-6.5 mol % VF-3.0 mol % PECo copolymer at 550°C and 125 MPa was heat-treated at 800°C for 6 h, the  $\sigma_s$  of Fe-Co-dispersed carbon increased from 157 to 213 e.m.u.  $g^{-1}$  (about 90% of the theoretical value) with an increase of  $H_c$  from 10 to 230 Oe.

Both a higher pyrolysis temperature of the copolymer and the subsequent heat treatment of as-prepared carbon promote not only the growth and crystallization of fine, superparamagnetic alloy particles but also a rearrangement of the crystal lattice of ferromagnetic alloy particles.

#### 4. Conclusions

Carbons dispersed with Fe-Co alloy could be synthesized by the pressure pyrolysis of organo-iron-organocobalt copolymers. The synthetic con-

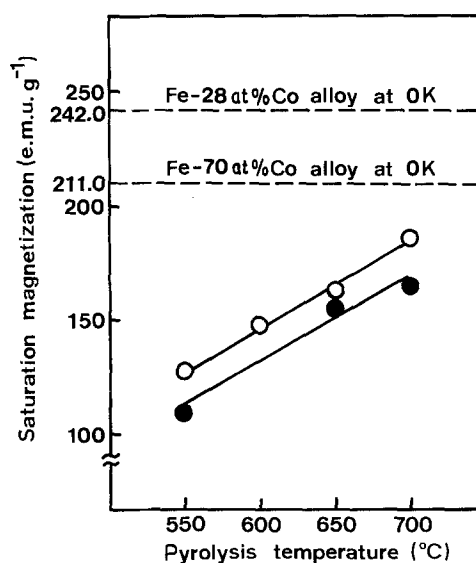


Figure 4 Saturation magnetization of Fe-Co-dispersed carbons synthesized from DVB-5.0 mol % VF-2.0 mol % PECo and DVB-2.0 mol % VF-5.0 mol % PECo copolymers at temperatures between 550 and 700°C at 125 MPa. (○) DVB-5.0 mol % VF-2.0 mol % PECo (Fe-29 at % Co); (●) DVB-2.0 mol % VF-5.0 mol % PECo (Fe-71 at % Co).

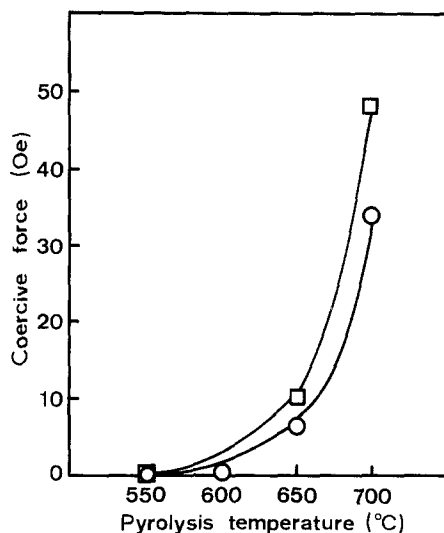


Figure 5 Coercive force of Fe-Co-dispersed carbons formed by pyrolysis of DVB-2.0 mol % VF-2.0 mol % PECO and DVB-5.0 mol % VF-2.0 mol % PECO copolymers at temperatures between 550 and 700°C at 125 MPa. (○) DVB-5.0 mol % VF-2.0 mol % PECO (Fe-29 at % Co); (□) DVB-2.0 mol % VF-2.0 mol % PECO (Fe-50 at % Co).

produce particles of Fe-Co alloy with a high regularity of crystal lattice.

3. Alloy-dispersed carbon with a high content of iron (Fe-29 at % Co) revealed a higher saturation magnetization than that of carbon dispersed with Fe-71 at % Co alloy.

4. The saturation magnetization and the coercive force of Fe-Co-dispersed carbon increased with increasing pyrolysis temperature of the copolymer because of the growth and crystallization of superparamagnetic and ferromagnetic particles dispersed in the carbon.

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