Synthesis and properties of nickel-dispersed carbons by pressure pyrolysis of nickelocene–divinylbenzene

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Nickel-dispersed carbon was synthesized by pressure pyrolysis of nickelocene–divinylbenzene at temperatures below 700° C at 125 MPa. The carbon so produced contained uniformly dispersed metallic nickel particles less than 40 nm in size with low crystallinity. The magnetization of nickelocene–divinylbenzene polymer increased abruptly at 280° C. The morphology of carbon changed from coalescing polyhedra to filaments via coalescing spherulites as the temperature increased from 550 to 700° C. Carbon tubes of 30 nm diameter were formed by pyrolysis of nickelocene–divinylbenzene at 650° C and 125 MPa. The Curie point of nickel-dispersed carbon was 360° C. The uniform dispersion of nickel with comparable crystallinity in the carbon matrix gave a linear relation between the saturation magnetization and the nickel concentration. The saturation magnetization of nickel-dispersed carbons synthesized at temperatures below 650° C and at 700° C were 60 and 85% of the theoretical value, respectively. The saturation magnetization of the nickel-dispersed carbon could be increased to reach 90% of the theoretical value with an increase in the crystallinity of dispersed nickel particles by subsequent heat treatment at 700° C for 7 h.

1. Introduction

Pressure carbonization of organic compounds for the synthesis of carbon materials is characterized by high yield and the controllability of the morphology of the carbon. Several workers [1–9] have reported effects of pressure on the nature of carbons synthesized by pressure pyrolysis of organic compounds and polymers.

Metal-dispersed carbons are synthesized by pressure pyrolysis of polymers containing organometallic compounds composed of carbon, hydrogen and metal. Marsh *et al.* [2] described the mesophase structure obtained from the pressure carbonization of a mixture of ferrocene and anthracene. Hirano *et al.* [3] synthesized carbon spherulites by the pressure pyrolysis of vinylferrocene copolymerized with divinylbenzene. Hirano *et al.* [10] demonstrated the synthesis of iron-dispersed carbons with various morphologies by pressure pyrolysis of organoiron copolymers.

The properties of metal-dispersed carbon have been found to depend strongly on the nature of both the carbon–metal bond of organometallic compounds and the carbon–carbon bond of the polymer matrix. In addition, both the concentration of metal in the starting polymer and the pyrolysis conditions, such as temperature and pressure, also influence the micro-phase liquid–liquid separation of a fluid phase and the morphologies of the resultant carbon matrix [10].

The present report deals with the synthesis and properties of nickel-dispersed carbons by pressure pyroly-sis of the polymer of nickelocene–divinylbenzene. The initial pyrolysis process was studied by the change of the magnetization of the pyrolysed compounds. The effects of pyrolysis temperature on the morphology of carbon matrix were also investigated. The properties of nickel particles dispersed in the carbon matrix were characterized by thermomagnetization and saturation magnetization.

2. Experimental procedures

Nickelocene (Cp_2Ni, where Cp = cyclopentadienyl) was prepared by the method described in the literature [11]. Commercially available divinylbenzene (DVB, a mixture of 55% *m*- and *p*-divinylbenzene and 45% ethylbenzene) was used for the preparation of starting organic polymer.

All pressure work was carried out with a hydro-thermal apparatus of the cold-seal type. Nickelocene was dissolved in divinylbenzene under nitrogen. The solution was sealed into a thin-walled gold capsule of 3.0 mm diameter and 50 mm length.

Various solutions of divinylbenzene containing nickelocene from 2.0 to 10.0 wt % were polymerized at 300° C and 100 MPa for 2 h and then pyrolysed at temperatures up to 700° C and 125 MPa. The heating rate was 10° C min^{-1} at a constant pressure at 125 MPa. The pressure was kept constant by releasing water as the pressure-transporting medium during heating. The pressure was measured with a calibrated Heise gauge and the temperature was measured with

a calibrated sheathed thermocouple set inside the pressure vessel. The sample was quenched after an experimental run.

The carbonized product was analysed by X-ray diffraction analysis. The as-prepared specimen was desorbed under vacuum for several hours at 250° C and then sealed into a quartz capsule under vacuum prior to heat treatment at 700° C for 7 h. The mixture solution of DVB–Cp$_2$Ni containing 3.0 wt % nickel as metallic element in a gold capsule was heat-treated at various temperatures from 200 to 350° C and 100 MPa. The magnetization of DVB–Cp$_2$Ni was then evaluated using a magnetic balance at room temperature. The relative magnetization was calculated using gold and ferrous ammonium sulfate FeSO$_4$(NH$_4$)$_2$SO$_4$·6H$_2$O, respectively, depending upon the magnitude of magnetization. The infrared (IR) spectrum of the nickel-containing polymer was measured by a KBr disc method.

The synthesized nickel-dispersed carbon was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and electron diffraction analysis. The thermomagnetization curve of nickel-dispersed carbon was measured with a magnetic balance from room temperature to 400° C. The as-prepared specimen was outgassed under vacuum for several hours at 250° C prior to the thermomagnetic measurement. A vibrating sample magnetometer (VSM) was employed for the evaluation at room temperature of the saturation magnetization and coercive force of synthesized nickel-dispersed carbons, in order to evaluate the state of nickel in the formed carbon matrix.

3. Results
3.1. Pyrolysis of nickelocene–divinylbenzene
3.1.1. X-ray diffraction studies
Pressure polymerization of DVB–6.0 wt % Cp$_2$Ni at 300° C and 100 MPa for 2 h gave a black, hard polymer which was further pyrolysed at 550° C and 125 MPa for 3 h to give a carbonized product.

The X-ray diffraction profile of the product was composed of broad diffraction lines having maxima at $2\theta = 25.5$ and 44.5° (CuKα), respectively (Fig. 1a).
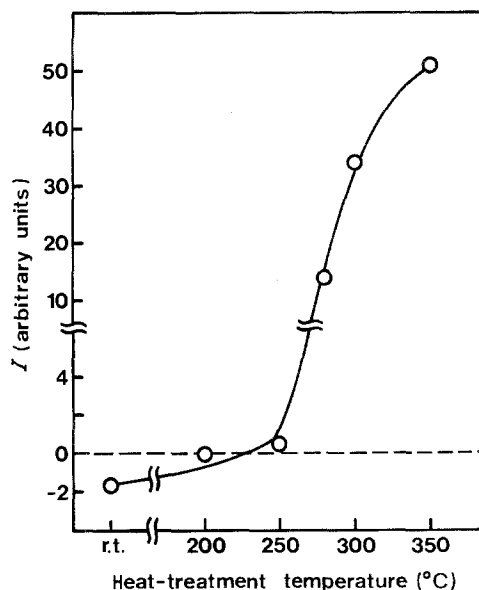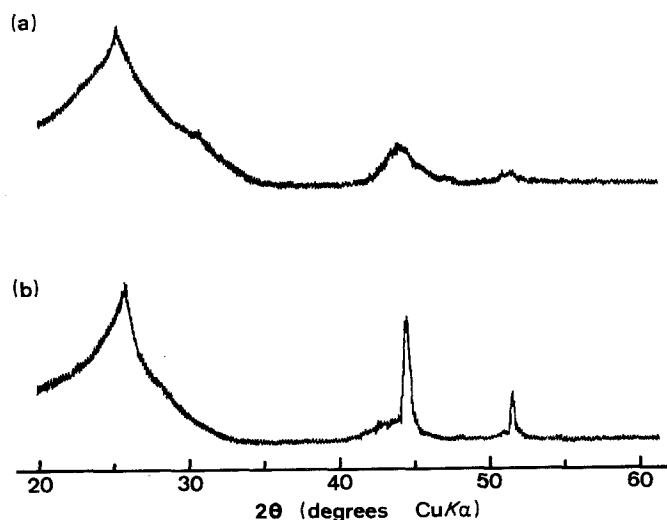
Figure 2 Magnetization of polymers containing 3.0 wt % nickel treated at various temperatures for 2 h under 100 MPa. r.t. = room temperature.

The former is ascribed to (0 0 2) diffraction of the turbostratic carbon, the latter corresponds to the (1 1 1) diffraction line of metallic nickel with low crystallinity. When the specimen was heat treated at 700° C for 7 h, the broad diffraction line of nickel with low crystallinity was replaced by a sharp (1 1 1) line at $2\theta = 44.5°$ with the appearance of (2 0 0) nickel diffraction at $2\theta = 51.8°$ as shown in Fig. 1b.

3.1.2. Magnetic properties of nickelocene–divinylbenzene
Fig. 2 illustrates the magnetization profiles of DVB–Cp$_2$Ni polymer containing 3.0 wt % Ni treated at various temperatures between 200 and 350° C. The divinylbenzene solution of nickelocene is diamagnetic at room temperature, because the larger amount of diamagnetic divinylbenzene dominates the magnetic property of the solution of nickelocene. The magnetic character of the DVB–Cp$_2$Ni polymer changed from diamagnetic to paramagnetic after heat treatment at 200° C and 100 MPa. The magnetization of the DVB–

Figure 1 X-ray diffraction profiles of nickel-dispersed carbons: (a) as-prepared nickel-dispersed carbon formed by pyrolysis of DVB–6.0 wt % Cp$_2$Ni at 550° C under 125 MPa, (b) after heat treatment of (a) at 700° C for 7 h.
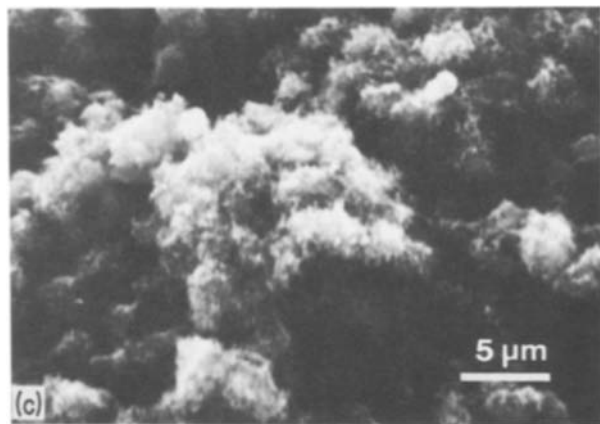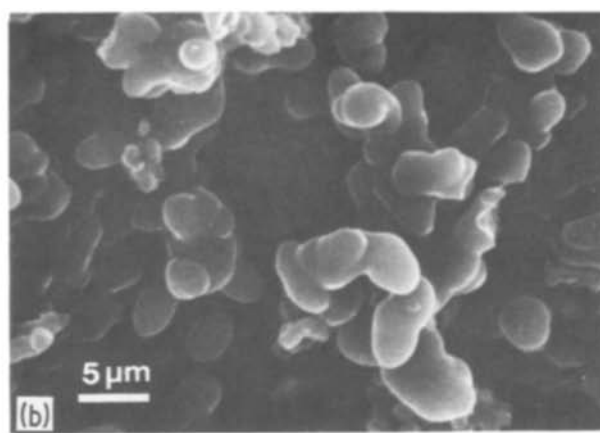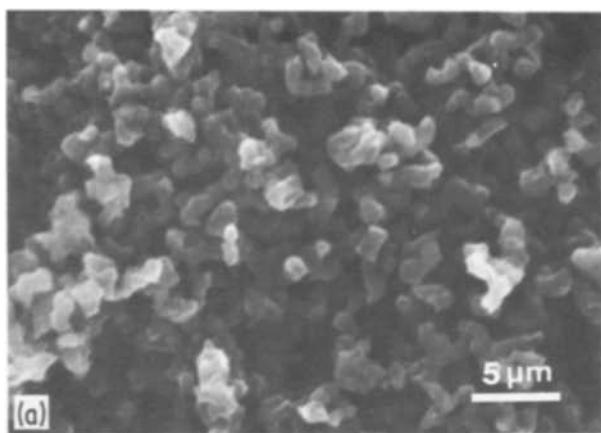
Cp_2Ni polymer increased by several orders of magnitude at 280° C after the gradual increase of magnetization from 200 to 250° C.

3.1.3. Infrared absorption

The absorption bands at 1100 and 1000 cm^{-1} in the IR spectra of the DVB–Cp_2Ni polymer can be attributed to cyclopentadienyl rings coordinated to nickel [12]. The DVB–Cp_2Ni polymer treated at 280° C and 100 MPa for 2 h showed no absorption bands at 1100 and 1000 cm^{-1}.

3.2. Morphology of synthesized nickel-dispersed carbon

3.2.1. Morphology

When DVB–2.0 wt % Cp_2Ni polymer was pyrolysed at 125 MPa for 3 h, morphological changes of the resultant carbons were as follows. Carbon with coalescing polyhedral morphology was obtained when the pressure pyrolysis was carried out at 550° C (Fig. 3a). The size of each polyhedron was less than 2 μm. Sharp edges of irregular polyhedra were rounded off to yield coalescing spherulites by pyrolysis at 600° C (Fig. 3b). The matrix of coalescing spherulites was accompanied by a small amount of filamentous carbon. As the pyrolysis temperature was increased to 650° C, the amount of filamentous carbon increased. The filamentous carbon formed at 700° C is shown in Fig. 3c.

As the concentration of nickelocene in a starting polymer increased from 2.0 to 9.7 wt % (from 0.62 to 3.0 wt % Ni) at 550° C, the carbon produced was composed of coalescing polyhedra, spherulites and filaments.

3.2.2. Microstructure of synthesized carbon

Fig. 4a represents the microstructure of carbon formed by the pyrolysis of DVB–6.0 wt % Cp_2Ni at 650° C and 125 MPa for 3 h. The dispersed black particles less than 40 nm in size were confirmed by electron diffraction to be nickel particles with f c c structure.

Fig. 4b shows the representative carbon filaments synthesized from DVB–7.8 wt % Cp_2Ni (2.4 wt % Ni) at 650° C and 125 MPa for 3 h. The majority of carbon filaments formed at 650° C were about 30 nm in diameter, with a few thick ones of about 40 nm diameter.
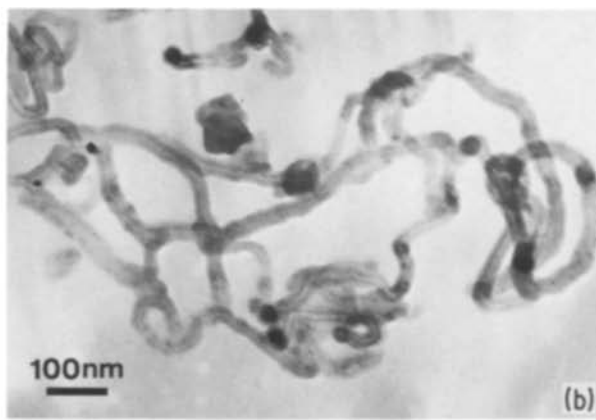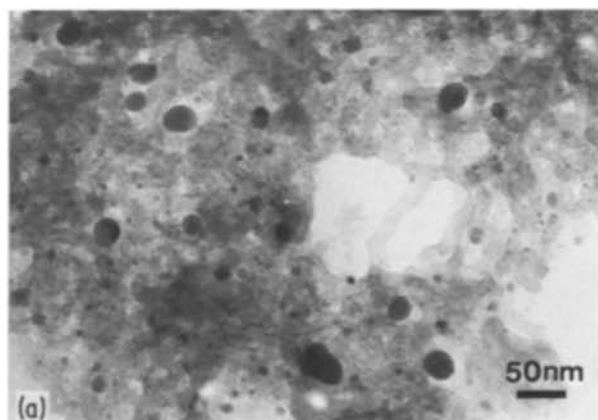

Figure 4 Microstructures of carbons dispersed with black particles of nickel: (a) carbon prepared from DVB–6.0 wt % Cp_2Ni by pyrolysis at 550° C under 125 MPa, (b) filamentous carbon synthesized by pyrolysis of DVB–7.8 wt % Cp_2Ni at 650° C under 125 MPa.
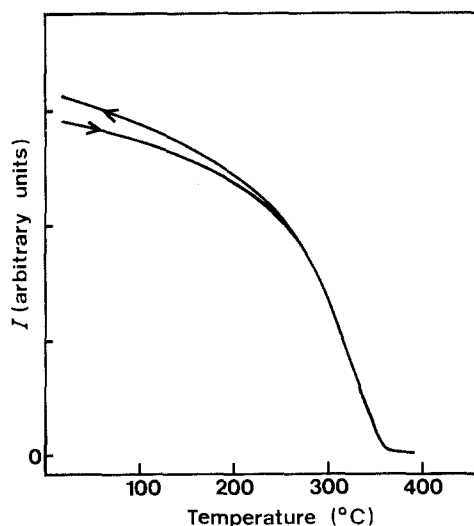
Figure 5 Thermomagnetization curve of nickel-dispersed carbon formed by pyrolysis of DVB–7.8 wt % Cp_2Ni at 650° C under 125 MPa.

Figure 7 Saturation magnetization of nickel-dispersed carbons synthesized by pyrolysis of DVB–6.0 wt % Cp_2Ni at temperatures between 550 and 700° C under 125 MPa.

The encapsulated nickel particles ranged from 10 to 30 nm in size.

3.3. Magnetic properties of nickel-dispersed carbon

3.3.1. Thermomagnetization behaviour

The thermomagnetization curve of Fig. 5 reveals the magnetic behaviour of nickel-dispersed carbon formed from DVB–7.8 wt % Cp_2Ni at 650° C and 125 MPa. The magnetization of the nickel-dispersed carbon decreased with increasing temperature and reached zero at 360° C. When the specimen was cooled to room temperature, its magnetization increased by about 8 % over that before the magnetization measurement.

3.3.2. Saturation magnetization

The observed saturation magnetization of nickel-dispersed carbon synthesized at 650° C and 125 MPa for 3 h is correlated with its concentration of nickel as shown in Fig. 6. Nickel-dispersed carbons showed a
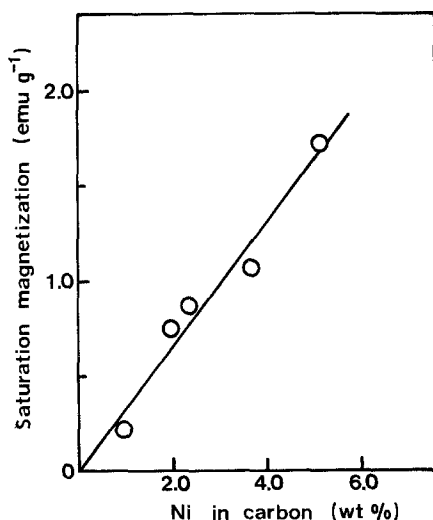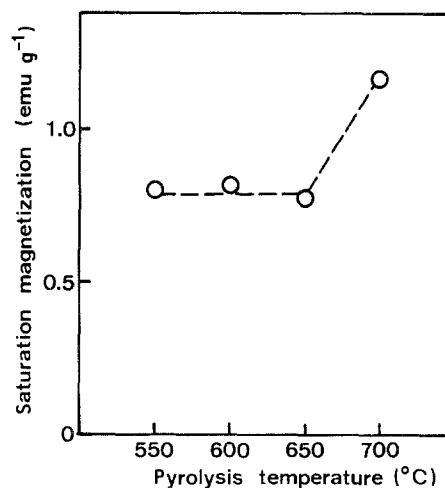
saturation magnetization of about 60 % of the theoretically calculated value. The coercive force of nickel-dispersed carbons was from 10 to 80 Oe.

Fig. 7 summarizes the saturation magnetization of nickel-dispersed carbon formed from DVB–6.0 wt % Cp_2Ni at temperatures between 550 and 700° C and 125 MPa for 3 h. The saturation magnetization of nickel-dispersed carbons was comparable when nickel-containing polymer was carbonized at temperatures between 550 and 650° C. However, pyrolysis at 700° C gave nickel-dispersed carbon with a higher saturation magnetization (85% of the theoretical value) compared with those obtained by pyrolysis at less than 650° C.

The carbon with dispersed 2.7 wt % Ni formed at 550° C and 125 MPa for 3 h was heat-treated at 700° C for 7 h. By this heat treatment, the saturation magnetization of the specimen increased from 0.85 to 1.32 emu g^{-1}, which corresponds to 90% of the calculated value based upon pure metallic nickel. Nickel particles with low crystallinity dispersed in the carbon matrix crystallized to highly crystalline nickel of f c c structure after heat treatment, as shown in Fig. 1.

4. Discussion

4.1. State of nickel in carbon matrix of pyrolysis product

Cementite has been formed in a carbon matrix by the pressure pyrolysis of organoiron copolymer at temperatures below 700° C [10]. On the other hand, metallic nickel particles disperse in a carbon matrix without any formation of nickel carbide by the pyrolysis of DVB–Cp_2Ni polymer under the same conditions, because nickel carbide is unstable above 320° C [13].

The Curie point of nickel-dispersed carbon is in agreement with that of pure nickel metal itself (358° C). It seems from the Curie point that nickel did not make any solid solution in the pressure-pyrolysed carbon formed at 650° C. The slight increase in magnetization after the thermomagnetic measurement is due to the growth and crystallization of dispersed superparamagnetic, fine nickel particles by heating during the magnetization measurement.

Figure 6 Saturation magnetization of nickel-dispersed carbons formed from DVB–Cp_2Ni polymers by pyrolysis at 650° C for 3 h under 125 MPa.

The proportional relation between the saturation magnetization and the concentration of nickel demonstrates the uniform dispersion of nickel with similar crystallinity in the carbon matrix synthesized below 650° C. An increase of the pyrolysis temperature to 700° C gave nickel-dispersed carbon with a higher saturation magnetization than those synthesized below 650° C, because the crystallinity of nickel particles was increased. Similarly, the heat treatment of as-prepared carbon played an important role, not only in the growth and the crystallization of superparamagnetic, fine nickel particles, but also in the increase of crystallinity of ferromagnetic particles.

4.2. Initial pyrolysis process

The degradation of the $DVB-Cp_2Ni$ polymer starts with the scission of the carbon–nickel bond, which generates paramagnetic species. The concurrent aggregation of the paramagnetic species proceeds rapidly at 280° C. Cobaltocene–DVB and vinyl-ferrocene–DVB polymers show a similar abrupt increase of the magnetization at 350 and 400° C, respectively. The mean bond dissociation energy $\bar{D}$ of the metal-ring bond of iron-triad metallocenes decreases in the order of $Cp_2Fe > Cp_2Co > Cp_2Ni$ as reported by Telnoi and Rabinovitch [14]. The thermal stability of iron-triad metallocenes decreases in the order $Cp_2Fe > Cp_2Co > Cp_2Ni$ in parallel with a decrease in $\bar{D}$ of the metal–cyclopentadiene ring bond. Therefore, the temperature of the abrupt increase of magnetization reflects the thermal stability of the metal–ring bond.

The analysis of IR spectra supports the idea that the interaction between nickel and the cyclopentadiene ring decreases considerably after heat treatment at 280° C.

These results suggest that the uniformity and size distribution of the dispersed metal are also adjustable by the control of chemical bonds in the starting organic and organometallic compounds.

4.3. Morphologies of synthesized carbons

The formation of isotropic carbon spherulites from polydivinylbenzene is explained by the decomposition of the polymer to oligomers and subsequent homogeneous liquid–liquid microphase separation between higher and lower molecular weight components [7].

Metal clusters originally dispersed in a liquid phase influence the liquid–liquid phase separation. The viscosity and density of the liquid phase and the dispersability of metal in the liquid phase depend mainly upon the temperature and concentration of the metal. This phase separation process determines that a heterogenous phase separation gives coalescing poly-hedral carbon at 550° C, while coalescing spherulites are formed by homogeneous phase separation at 600° C as found in the case of spherulitic carbon formation [7].

The various types of filamentous carbon have been synthesized by catalytic decomposition of carbon-containing gases at pressures of 10^5 Pa or less [15]. Several mechanisms have been proposed to explain the filament growth [16–19].

The formation of gaseous component increases with increase of the pyrolysis temperatures to 650° C, though pressure suppresses the generation of gases mainly originating from the lower molecular weight substances produced during the phase separation. Carbon tubes grow on contact with active nickel particles by a similar mechanism [16, 18, 19] including the supply of carbon followed by its diffusion through the surface layer of metal.

The diameter of filaments depends upon the reaction conditions such as the size of catalyst particles [20], growth temperature [21] and time [19]. The pressure pyrolysis of $DVB-Cp_2Ni$ polymer at 650° C gave thinner filaments than those obtained by catalytic decomposition of carbon-containing gases [20, 22]. The size of metal particles formed by the aggregation of paramagnetic species originally dispersed as metallocene is less than 40 nm, which is smaller than that obtained by fragmentation of metals [23]. Therefore, the diameter of filaments synthesized by pressure pyrolysis also reflects the size of the catalyst particle itself. A more detailed study of the mechanism of forming filamentous carbon by pressure pyrolysis is in progress.

5. Conclusions

The polymer of nickelocene–divinylbenzene was pyrolysed under pressure to synthesize carbons with finely dispersed nickel. The formation process and the properties of nickel-dispersed carbons were studied. The summarized results are as follows:

1. Nickel-dispersed carbon was directly synthesized by pressure pyrolysis of a mixture of nickelocene–divinylbenzene without formation of nickel carbide.

2. Nickelocene–divinylbenzene underwent degradation of the nickel–carbon bond at low temperature such as 280° C, which reflects the small mean dissociation energy of the nickel–carbon bond.

3. The morphology of synthesized carbon depended upon the pyrolysis temperature of the starting polymer. The participation of the gaseous phase of hydrocarbons with lower molecular weight in the pyrolysis process resulted in the formation of nickel-dispersed tubulous carbon by pressure pyrolysis at 650° C and 125 MPa.

4. The saturation magnetization of as-prepared nickel-dispersed carbon revealed 60% of the theoretical value, which resulted from the low crystallinity of nickel in the carbon formed below 650° C.

5. The growth and crystallization of superparamagnetic and ferromagnetic nickel particles by heat treatment increased the saturation magnetization of nickel-dispersed carbon up to 90% of the theoretically calculated value.

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