Synthesis of nickel ferrite-dispersed carbon composites by pressure pyrolysis of organometallic polymer

S.-I. HIRANO, T. YOGO, K.-I. KIKUTA, M. FUKUDA
Department of Applied Chemistry, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

Nickel ferrite-dispersed carbon could be synthesized by pressure pyrolysis of divinylbenzene (DVB)–vinylferrocene (VF)–nickelocene (Cp_2Ni) polymer in the presence of water under 125 MPa and at temperatures below 700 °C. By heat treatment at 550 °C with water, nickel ferrite particles could be dispersed finely in the carbon matrix, although a small amount of nickel–iron carbide also began to form above 600 °C. The morphologies of the carbon particles formed were observed to be polyhedral, coalescing spherulitic and spherulitic. When 30 wt % H_2O, spherulitic carbons a few micrometres in diameter were prepared, in which nickel ferrite particles from 10–30 nm were dispersed in the carbon matrix. The saturation magnetization of carbon composites formed from DVB–3.0 mol % Cp_2Ni–6.0 mol % VF and 20 wt % H_2O at 550 °C was about 30 e.m.u. g^{-1} and increased with pyrolysis temperature. The coercive force of the carbon composite was 120 Oe and was affected by the amount of added water using pressure pyrolysis. Thermomagnetic measurement shows that the Curie temperature of nickel ferrite-dispersed carbon was about 580 °C.

1. Introduction

Pressure pyrolysis is characterized by a high yield of carbon and controllability of the morphology of the carbon products. Hirano et al. [1] synthesized mesophase spherulitic carbon by pressure pyrolysis of anthracene, p-terphenyl and a mixture of these, using a hydrothermal apparatus. Hirano et al. [2] demonstrated that pyrolysis under various pressures of 30–200 MPa could produce many kinds of carbon morphology, including isotropic carbon spherulites. Carbon composite containing fine metal or metal compound particles, such as iron [3, 4], cobalt [5], nickel [6], iron–cobalt alloy [7], iron–carbide [8, 9], magnetite [10], could be synthesized by pressure pyrolysis of divinylbenzene copolymerized with vinylferrocene, phenylethynyl cobaltocene, etc. Both the metal–carbon and carbon–carbon bondings of the starting organometallic polymer influence the carbonization process so that the selection of starting material is one of the most important factors in controlling the morphology and the nature of the resultant carbons.

Metal oxide particles, such as magnetite and nickel ferrite, are quite stable compared to metal particles under oxidative conditions. These magnetic particles-dispersed carbons have many attractive applications, such as electromagnetic wave shields, because ferrite particles as magnetic materials are uniformly dispersed in carbon to produce an electrically conductive material. Moreover their composites are potential materials for catalysts and magnetic toners.

This paper describes the synthesis and the properties of nickel ferrite-dispersed carbons by pressure pyrolysis of organometallic polymers formed from divinylbenzene (DVB) solutions of vinylferrocene (VF) and nickelocene (Cp_2Ni). The influence of the pyrolysis conditions and the concentration of metal components on the morphologies and magnetic properties of the carbon composites were also studied.

2. Experimental procedure

Nickelocene (Cp_2Ni) and vinylferrocene (VF) were prepared by the methods described in the literature [11, 12]. Commercially available divinylbenzene (DVB, a mixture of m- and p-divinylbenzene and 45% ethylbenzene, diethylbenzene) was used as a starting organic compound for polymerization. Cp_2Ni and VF corresponding to the compositions of nickel ferrite (Fe/Ni ratio = 2) were dissolved in divinylbenzene under a nitrogen atmosphere. The concentration of metallocenes in DVB was adjusted to be from 0.5–3.0 mol % for Cp_2Ni and from 1.0–6.0 mol % for VF. The solution of Cp_2Ni–VF–DVB was sealed in a thin-walled gold capsule and then polymerized with a hydrothermal apparatus of the cold-seal type at 300 °C for 2 h under 100 MPa pressure.

The polymer dispersed with organometallic molecules was resealed in a gold capsule (5 mm diameter and 60 mm long) with various amounts of water, and then pyrolysed under pressure from 30–125 MPa at temperatures between 550 °C and 700 °C for 3 h. The

temperature was raised at a rate of 10 °C min^{-1}. The pressure was monitored with a calibrated Heise gauge, and kept constant by releasing water as a pressure-transporting medium during heating. The temperature was controlled with a calibrated sheathed thermocouple.

The carbonized products were characterized by X-ray diffraction analysis (XRD) with CuK_α radiation using a monochrometer. The lattice constant of ferrite was determined from its (4 4 0) and (5 1 1) diffractions with highly pure tungsten as an internal standard. The saturation magnetization and coercive force were measured with a vibrating sample magnetometer (VSM) at room temperature. The saturation magnetization of ferrite-dispersed carbon was converted to the value per gram of ferrite. The thermomagnetization curves of the carbon composites were determined using a magnetic balance (MB). The microstructure of the carbon and particles of nickel-ferrite was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

3. Results and discussion

3.1. Synthesis of nickel ferrite-dispersed carbons

The XRD profiles of magnetic particles-dispersed carbons pyrolysed at various temperatures are shown in Fig. 1. When DVB-3.0 mol % Cp$_2$Ni-6.0 mol %VF was pyrolysed without water, the XRD profile consisted of only carbon (0 0 2) and (1 0) diffractions centred at about $2\theta = 25°$ and 44.5° (Fig. 1a). No diffractions of metal and metal compounds were observed in the profile. Fig. 1b shows the XRD pattern of the specimen synthesized from DVB-3.0 mol % Cp$_2$Ni-6.0 mol % VF and 20 wt % H$_2$O at 550 °C and 125 MPa. All sharp reflections are assigned to those of nickel ferrite (NiFe$_2$O$_4$). The coexistent water oxidized atomic metals in the polymer to disperse nickel ferrite in the carbon matrix during pyrolysis at 550 °C. Pressure pyrolysis at higher temperature improved the crystallinity of the nickel ferrite particles, although nickel–iron carbide was partly formed as a by-product through the reduction of ferrite by carbon above 600 °C (Fig. 1c).

Nickel ferrite has a cubic crystal structure and a lattice constant of 833.9 pm, while the lattice constant of nickel ferrite particles in the carbon composite prepared at 650 °C was measured to be 837 pm. This value was confirmed to be the middle value between nickel ferrite, NiFe$_2$O$_4$, and magnetite, Fe$_3$O$_4$ ($a_o = 839.6$ pm), which indicates that the composition of the nickel ferrite produced corresponds to a solid solution with a larger amount of iron compared to the stoichiometric nickel ferrite. The carbonized product at 600 °C included nickel–iron carbide referred to the X-ray diffraction pattern at $2\theta = 44.2°$ (Fig. 1c), and showed the corresponding Curie temperature at 390 °C in the thermomagnetization curve (see Fig. 4 below). The Curie temperature of nickel–iron alloy changes from 350 °C to 612 °C depending upon the Ni/Fe ratio [13]. The inclusion of carbon in pure nickel lowers the Curie temperature from 358 °C to
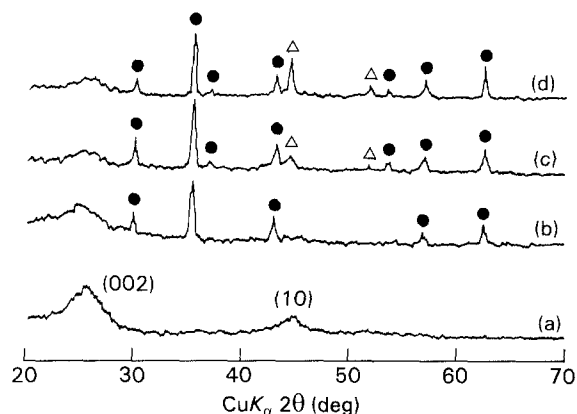

Figure 1 XRD profiles of nickel ferrite-dispersed carbons synthesized by pressure pyrolysis of DVB-3.0 mol % Cp$_2$Ni-6.0 mol % VF polymer at various temperatures under 125 MPa: (a) pyrolysed in the absence of water at 550 °C; (b) – (d) pyrolyzed in the presence of 15 wt % H$_2$O at (b) 550° C, (c) 600 °C and (d) 700 °C. ($\bullet$) NiFe$_2$O$_4$, ($\triangle$) (Ni,Fe)$_x$C.

320 °C [14]. These results indicate that the cubic lattice of nickel–iron carbide consists mainly of nickel iron, and is partially substituted for a small amount of iron with the inclusion of carbon. The nickel ions excluded from iron-rich ferrite are considered to be incorporated in nickel–iron carbide produced by pyrolysis above 600 °C.

3.2. Morphologies and microstructures of nickel ferrite-dispersed carbons

Polymers of DVB-Cp$_2$Ni-VF were pyrolysed in the presence of 15-35wt % H$_2$O at 550 °C under 125MPa. Fig. 2a shows the typical morphology of nickel ferrite-dispersed carbon synthesized from 3.0 mol % Cp$_2$Ni-6.0 mol % VF polymer with addition of 20 wt % H$_2$O. Fig. 2b and c also show the morphologies of carbon formed from 0.5 mol % Cp$_2$Ni-1.0 mol % VF polymer with 20 wt % H$_2$O and DVB-3.0 mol % Cp$_2$Ni-6.0 mol % VF polymer containing 30 wt % H$_2$O, respectively. The carbon particles formed from polymer having a high metal content decreased in size of the spherulitic carbons. Coalescing spherulitic carbons containing 3.0 mol % ferrite had a comparatively small diameter of about 1 μm (Fig. 2c). whereas the particle sizes increased to 30-40 μm on decreasing the metal concentration to 0.5 mol % in the parent polymers as shown in Fig. 2b.

The morphologies of the resultant carbon were affected by various factors, such as pyrolysis pressure and temperature, amount of water and concentration of metal. The coexistent supercritical water contributed markedly to the liquid–liquid microphase separation in this system, leading to the control of morphologies [1]. Pyrolysis temperature also influenced the solubility of metal particles, viscosity, density and liquid–liquid phase separation. Spherulitic carbons were reported to form by phase separation of the fluid phases between the higher molecular weight component containing metal and the lower molecular weight component during pyrolysis. Insoluble carbon might precipitate from liquid phases on to metal particles, which acted as nuclei for the formation of
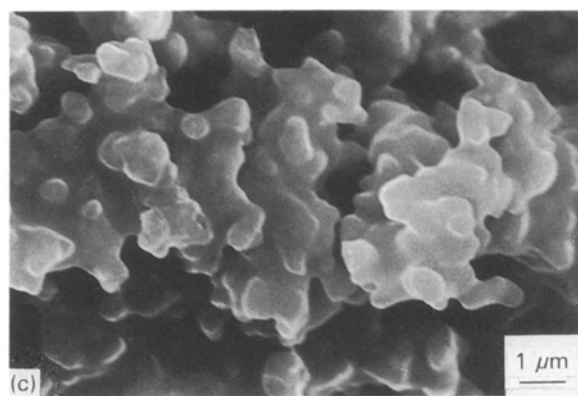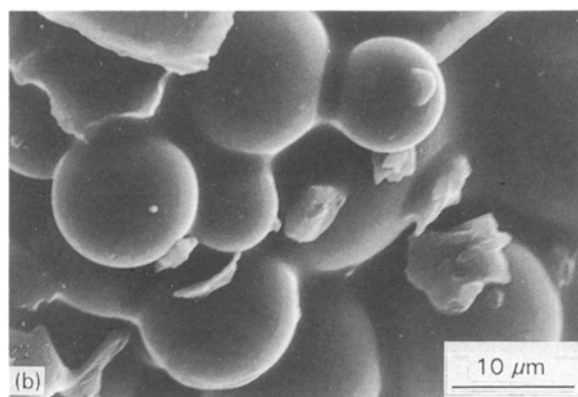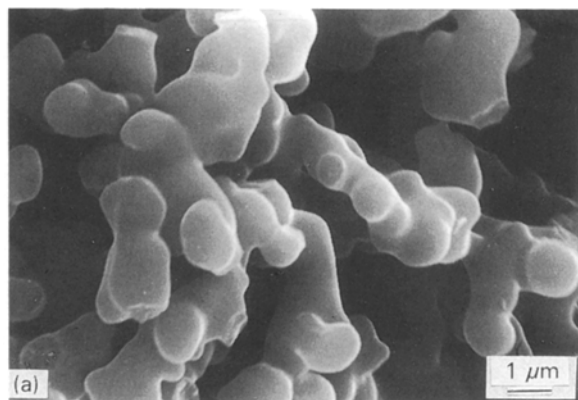
Figure 3 Microstructure of nickel ferrite-dispersed carbon synthesized by pressure pyrolysis of DVB–3.0 mol %Cp$_2$Ni–6.0 mol % VF polymer at 550 °C and 15 wt % H$_2$O under 125 MPa.

Figure 2 Morphologies of nickel ferrite-dispersed carbons synthesized by pressure pyrolysis of DVB–Cp$_2$Ni–VF polymers at 550 °C. (a) DVB–3.0 mol % Cp$_2$Ni–6.0 mol % VF polymer and 20 wt % H$_2$O, (b) DVB–0.5 mol % Cp$_2$Ni–1.0 mol % VF polymer and 20 wt % H$_2$O, (c) DVB–3.0 mol % Cp$_2$Ni–6.0 mol % VF polymer and 30 wt % H$_2$O.

spherulitic carbon. When starting polymers are comprised of high concentrations of metallocenes, a large number of nuclei for carbonization are formed during pyrolysis. The higher molecular weight component containing these nucleation sites could be produced at many points in the phase of the lower molecular weight component. The high metal content, therefore, results in the formation of smaller individual spherulitic or polyhedral carbon particles. As the amount of added water increased, the increased difference in density and viscosity between the lower molecular weight phase and the higher molecular weight phase is considered to change the phase separation, yielding spherulitic carbons rather than polyhedral carbons.
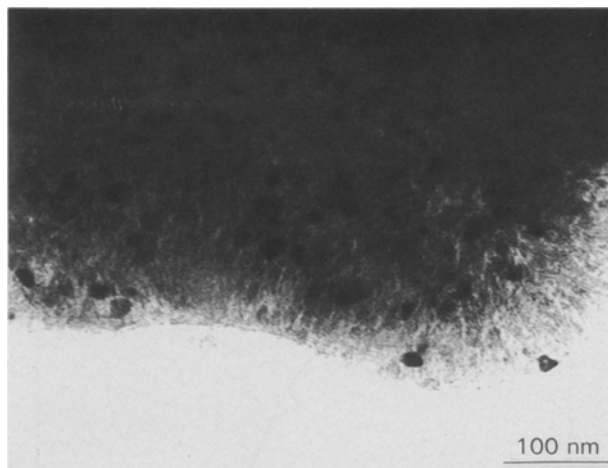
Fig. 3 shows the microstructures of nickel ferrite-dispersed carbons synthesized from DVB–3.0 mol % Cp$_2$Ni–6.0 mol % VF polymers at 550 °C under 125 MPa. The water content in the starting mixture with the polymer was 15 wt %. The black particles in Fig. 3 were nickel ferrite finely dispersed in the carbon matrix. The size of the ferrite particles was unaffected by the concentration of water. The diameter of the ferrite particles ranged from 15–25 nm, which corresponds to the size of a magnetic single domain.

3.3. Magnetic properties

Fig. 4 illustrates the thermomagnetization curve of nickel ferrite-dispersed carbon formed from DVB–3.0 mol % Cp$_2$Ni–6.0 mol % VF polymers with 15 wt % water at 600 °C and 125 MPa for 3 h. The magnetization decreased on heating and the Curie points were recognized at 585 ° and 400 °C, which were in agreement with those of nickel ferrite and nickel–iron carbide, respectively. No other magnetic materials in the carbon matrix were observed in the thermomagnetic curves.

The saturation magnetization of the nickel ferrite-dispersed carbons synthesized at temperatures from 550–700 °C is shown in Fig. 5. The saturation magnetization increased with increasing pyrolysis temperature. The saturation magnetization of carbon composite pyrolysed at 550 °C and 125 MPa in the presence of 20 wt % water was 30 e.m.u g^{-1} and increased up to 58 e.m.u g^{-1} at 700 °C. This value of the saturation magnetization at 550 °C is 50% of the theoretical value of pure nickel ferrite itself, 56 e.m.u g^{-1}, because nickel ferrite particles were not perfectly crystallized in the carbon matrix and the magnetic moments of iron were not perfectly antiparallel between tetragonal sites and octahedral sites in the spinel structure. Above 600 °C, nickel ferrite begins to be reduced to nickel–iron carbide, resulting in the dispersion of two kinds of magnetic materials in a carbon matrix, as shown in Figs 1 and 4. Nickel–iron
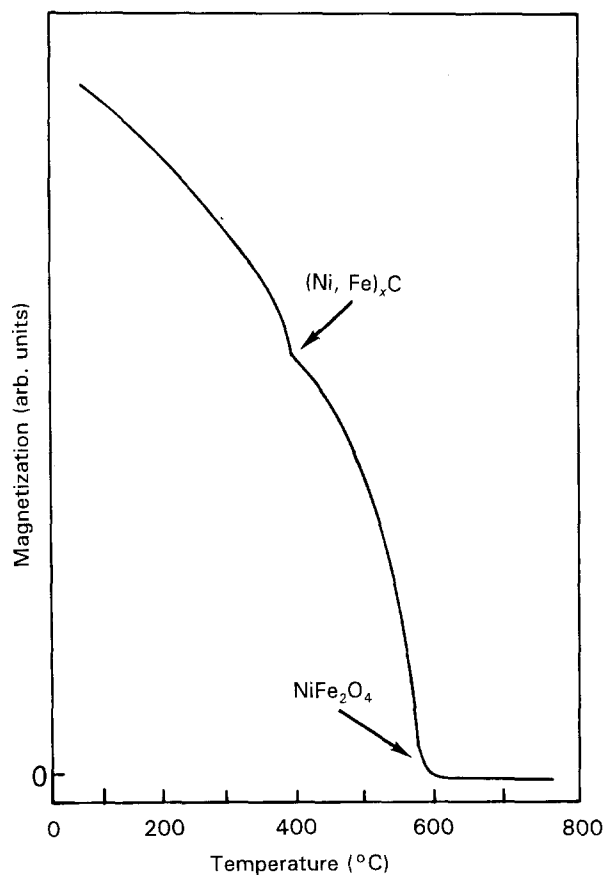
Figure 4 Thermomagnetization curve of nickel ferrite-dispersed carbon synthesized from DVB–3.0 mol % Cp₂Ni–6.0 mol % VF polymer with 15 wt % H₂O at 600 °C and 125 MPa.

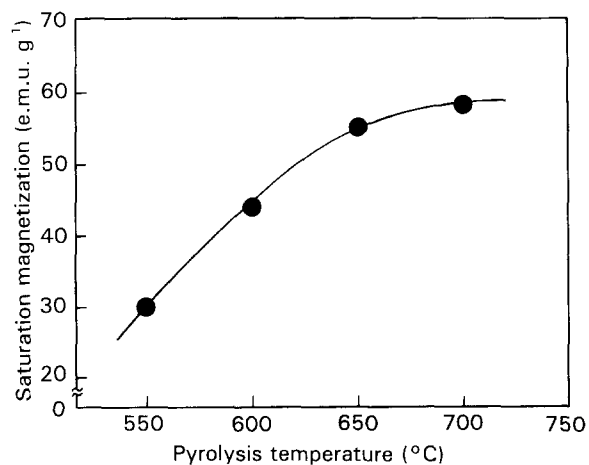Figure 5 Saturation magnetization of nickel ferrite-dispersed carbons pyrolysed at various temperatures and 125 MPa (DVB–3.0 mol % Cp₂Ni–6.0 mol % VF polymer and 15 wt % H₂O and 125 MPa).

carbide of cubic symmetry is composed of a higher content of nickel than the stoichiometry, because nickel ferrite in the carbon matrix is rich in iron as shown in Section 3.1. Therefore, the saturation magnetization of nickel–iron carbide is as high as that of nickel (55.1 e.m.u g⁻¹), which is comparable to the value of nickel ferrite. As the pyrolysis temperature was raised, the amount of nickel–iron carbide increased and, consequently, the composition of nickel ferrite became richer in iron, which shifted the satura-
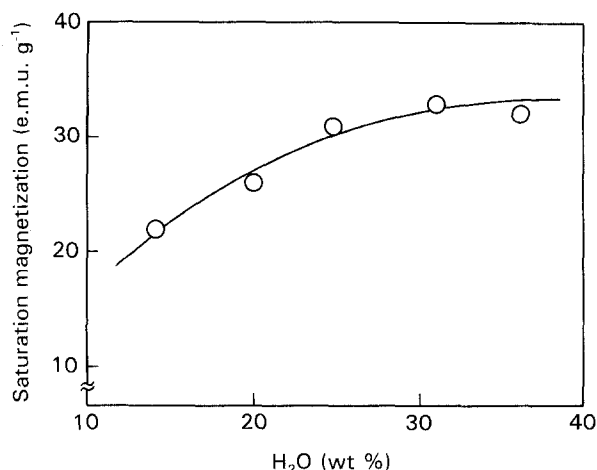

Figure 6 Saturation magnetization of nickel ferrite-dispersed carbons pyrolysed in the presence of various amounts of water at 550 °C and 125 MPa (DVB–3.0 mol % Cp₂Ni–6.0 mol % VF polymer).
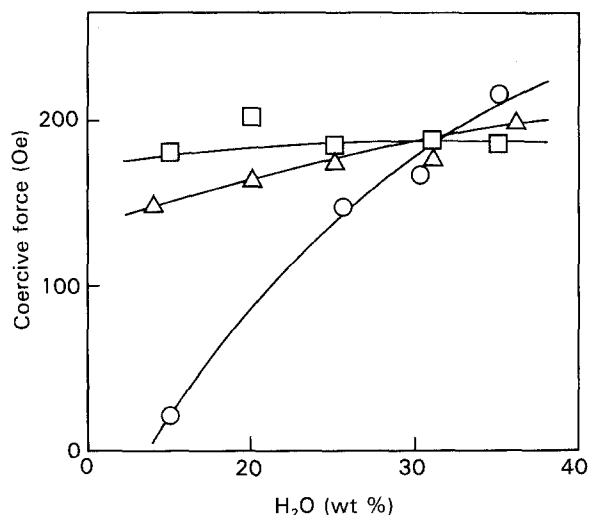

Figure 7 Coercive force of nickel ferrite-dispersed carbons pyrolysed in the presence of various amounts of water at 550 °C and 125 MPa. (□) DVB–0.5 mol % Cp₂Ni–1.0 mol % VF polymer. (△) DVB–1.5 mol % Cp₂Ni–3.0 mol % VF polymer. (○) DVB–3.0 mol % Cp₂Ni–6.0 mol % VF polymer.

tion magnetization to a value approaching that of magnetite and higher than nickel ferrite. This is the most significant reason for increasing the saturation magnetization of carbon composites.

Fig. 6 shows the saturation magnetization of nickel ferrite-dispersed carbons formed from DVB–3.0 mol % Cp₂Ni–6.0 mol % VF at 550 °C with various amounts of water. Nickel and iron compounds are easily oxidized to nickel ferrite by the addition of water, as shown in Fig. 1. The saturation magnetization increases with the amount of water, which also increases the crystallinity of the nickel ferrite particles.

Fig. 7 shows the coercive force of nickel ferrite-dispersed carbon pyrolysed from DVB–3.0 mol % Cp₂Ni–6.0 mol % VF polymer with various amounts of water. The coercive force of carbon composite synthesized in the presence of 15 wt % H₂O was a low value of 20 Oe. The coercive force of carbon composites containing a higher concentration of metal

increased with increasing water content and reached 220 Oe at 35 wt % H_2O. However, the coercive force is independent of the amounts of added water at low metal concentrations of 0.5 mol % in the starting polymers, and showed a constant value of about 180 Oe. Supercritical water promoted the crystallization of nickel ferrite and raised both the saturation magnetization and the coercive force of the specimens.

4. Conclusions

The organometallic polymer formed from divinylbenzene–nickelocene–vinylferrocene was pyrolysed under pressure in the presence of water to synthesize nickel ferrite-dispersed carbon. The results are summarized as follows.

1. By pressure pyrolysis at 550 °C, only nickel ferrite particles were dispersed in the carbon matrix, although nickel–iron carbide was produced together with nickel ferrite above 600 °C.

2. The morphology and the size of the resultant carbon particles depended upon the pyrolysis temperature, the amount of added water and the metal content in a starting polymer.

3. The saturation magnetization of nickel ferrite-dispersed carbon composite was 30 e.m.u g^{-1} at 550 °C, and increased up to 58 e.m.u g^{-1} with increasing pyrolysis temperature. The maximum coercive force of nickel ferrite-dispersed carbon composite was 220 Oe, which was affected by the amount of added water.

References

1. S. HIRANO, I. OHTA and S. NAKA, *J.Chem. Soc. Jpn* **1981** (1981) 1356.
2. S. HIRANO, F. DACHILLE and P. L. WAKER Jr., *High Temp. High Press.* **5** (1973) 207.
3. S. HIRANO, T. YOGO, H. SUZUKI and S. NAKA, *J.Mater. Sci.* **18** (1983) 2811.
4. T. YOGO, S. NAKA and S. HIRANO, *ibid.* **24** (1989) 2071.
5. S. HIRANO, T. YOGO, N. NOGAMI and S. NAKA, *ibid.* **21** (1986) 225.
6. T. YOGO, E. TAMURA, S. NAKA and S. HIRANO, *ibid.* **21** (1986) 941.
7. S. HIRANO, T. YOGO, K.KIKUTA and S. NAKA, *ibid,* **21** (1986) 1951.
8. T. YOGO, H. YOKOYAMA, S. NAKA and S. HIRANO, *ibid.* **21** (1986) 2571.
9. T.YOGO, S. NAKA and S.HIRANO, *ibid.* **22** (1987) 985.
10. *Idem, ibid.* **24** (1989) 2115.
11. W. L. JOLLY and D.J. CHAZEN, *Inorg. Synth* **11** (1968) 122.
12. F. S. ARIMOTO and A. C. HAVEN Jr., *J. Amer. Chem. Soc.* **77** (1955) 6295.
13. M. HANSEN and K. ANDREKO (eds), "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958) p. 677.
14. S. MÜLLER and H. LANGE, *Z. Inorg. Phisik XVII* **3** (1964) 142.