

STRUCTURAL FEATURES AND MAGNETIZATION PROPERTIES OF NANO-IRON/CARBON COMPOSITE FROM PETROLEUM RESIDUE AND FERROCENE

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Introduction

The composite of metal nanoparticles dispersed in carbon matrix generally exhibit outstanding properties and can be widely used as electronic, electric, and magnetic materials, oxidation/reduction catalyst, adsorbents and antibacterial agents, etc., [1] depending on the kinds and structures of metals and carbons. There are some reports about the synthesis of metal-dispersed carbon by pressure pyrolysis from soluble organometallic polymers [2], macromolecular-metal complexes and blends of coal tar pitch with metal complexes [3] at 400-1400 °C for 1-2days in nitrogen atmosphere. However, the above process is very complicated including polymer synthesis, dissolving, evaporation and carbonization and mostly need very high pressures and temperatures (above 600 °C and 100MPa) [2,4,5].

Although Huttinger et al [6] has reported the preparation of mesophase pitch from coal tar pitch using ferrocene as the catalyst, the morphology and dispersed state of iron in carbon were not researched. In previous paper [7] the preparation of nano-iron dispersed carbon from petroleum residue in the presence of ferrocene has been reported. In this paper, the structural features and magnetization properties of this nano-iron/carbon

composite were investigated using transmission electron microscope (TEM), X-ray diffraction (XRD) and Vibrating Sample Magnetometer (VSM).

Experimental

Table 1 shows the elemental analysis of the refined petroleum residue (RPR). The mixture of ferrocene (Analytically Pure) and petroleum residue in a certain amount (from 3wt% to 20wt% based on the RPR) was added to a 1L autoclave. After excluding the air in the vessel by flow N₂, the reaction vessel was sealed and heated to 420 °C at the rate of 100 °C/h keeping for 2~8h by continuous mechanical stirring at the auto-pressure with the biggest pressure of about 8MPa. When the reaction was over, the product was extracted with pyridine many times to remove the soluble fraction of mesophase pitch completely and the pyridine insoluble fraction was used as the desired sample. Then by further heat treatment (800-1000 °C) the nano-iron particle dispersed carbon was obtained.

X-ray diffraction analysis was performed in a Rigaku D/max-2400 system using CuK_α radiation ($\lambda=1.5406\text{\AA}$) with spinning width of 10 to 90 degree. Transmission electron microscope was run on Hitachi H-800.

Coercivity and saturation magnetization were measured by a Vibrating Sample Magnetometer (VSM, LDJ 9600)

Table 1 Element content of the petroleum residue (wt%)

C	H	H/C	N	O	S
88.86	9.42	1.26	≤0.3	0.42	0.82

Results and discussion

1. Morphology and structure of nano-iron particle / carbon composite

Fig.1 shows the TEM images of as-prepared and carbonized extracted mesophase pitch powders. It can be seen that nano particles of Fe (diameter, 20-80nm) are dispersed uniformly in the resulting carbon matrix. By heat treatment (Fig.1 (b)) at 850°C, the diameter of iron particles becomes larger than that of un-heat treated sample, which may be attributed to the particle aggregation each other through further heat treatment.

The extraction products (pyridine insoluble fractions) were analyzed by X-ray diffraction (XRD). The typical results are shown in Figs.2. From Fig.2, we can see that, when the ferrocene additions are 3% and 6%, the states of iron dispersed in carbon are Fe-O (Fe_3O_4) and Fe-S (Fe_{1-x}S , $1 > x > 0$) compounds, however in Fig.2(c) when the ferrocene content is 10%, the main iron present compounds are α -Fe, Fe-S and Fe-O. In the petroleum residue, there are some amount of sulfur and oxygen as shown in Table1. The existence of more reactive sulfur- and oxygen-containing compounds can easily react with nano-iron particles firstly. During the pyrolysis, the

decomposition of ferrocene results in the formation of elemental iron. Sulfidation and oxidization of iron may occur simultaneously and a part of iron is obviously converted into iron sulfide and oxide.

2. Magnetic property of nanoiron / carbon composite

Magnetization curve observed at the room temperature (25°C) on the nano-iron/carbon composites prepared at 420°C for 5h with different ferrocene contents are shown in Fig. 3 and Fig. 4, respectively. From these two plots, we can see that with the increase of nano-iron particles, the saturation magnetization σ_s (from 6.60 to 15.68 emu/g), coercive force H_c (from 202.4 to 273.9 Oe) and remnant magnetization σ_r (from 1.37 to 3.22 emu/g) were all increased. It is suggested that the nano-iron particles are the attributor to the magnetization. From these plots, it can be seen that there is a small hysteresis indicating that iron-carbon particle/carbon is ferromagnetic material which can be used as information recorder materials.

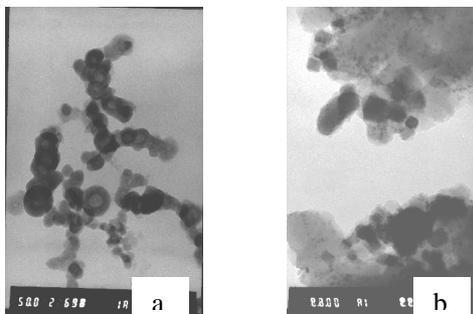
Conclusion

The diameter of the resulting iron particles uniformly dispersed in carbon matrix is about 20~80nm, which is dependent upon the ferrocene addition content and condensation variables, respectively. With the increase of ferrocene addition content, the size of iron particles is becoming larger from the TEM observation. Besides the formation of α -Fe, the other iron residing forms such as Fe_3O_4 , Fe_{1-x}S and Fe_2O_3 were also presented in the iron/carbon system investigated from XRD patterns, indicating the sulfidation and oxidation between the iron and sulfur and oxygen existed in the petroleum residue

may occurred. The material of nano-iron particles dispersed in carbon shows the soft-magnetic properties and may be used as magnetic recorder materials.

References

[1] E. Yasuda □ Tanso □ 136 □ 1989 □ 57 (Japanese).
 [2] T. Yogo, S. Naka and S. Hirano., J. Mater. Sci. 24 (1989) 2071.
 [3] M. Higashi, H. Tamai, F. Nishiyama and H. Yasuda, Tanso (182) (1998) 79 (Japanese).
 [4] Y. Yogo, S. Naka and S. Hirano., J. Mater. Sci. Letters 24 (1989) 2115.
 [5] Y. Yogo, E. Tamura, S. Naka and S. Hirano., J. Mater. Sci. 21 (1986) 941.
 [6] M. Bernhauer, M. Braun and K. J. Huttinger, Carbon 32 (1994) 1073.
 [7] H. Song, X. Chen and X. Chen, 1st World Conf. On Carbon, 9-13 July, 331(2000, Berlin, Germany)



composite obtained at 420□ soaking for 5h from petroleum residue in the 3% content of ferrocene of (a) as prepared and (b) heat treated at 850□

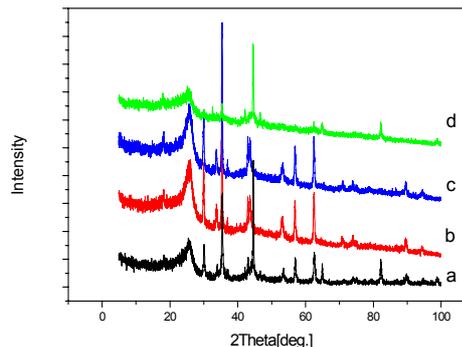


Fig. 2 XRD patterns of nano-iron/carbon composites with different ferrocene addition (a) 3%, (b) 6%, (c) 10% and (d) 20%

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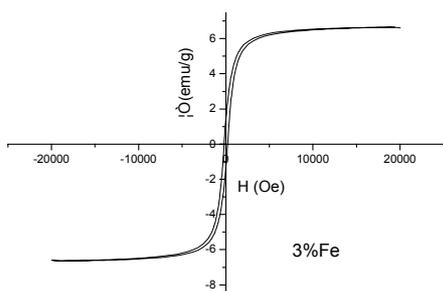


Fig. 3 Magnetization curve of nano-iron/carbon composite prepared at 420□-5h in the presence of 3% ferrocene

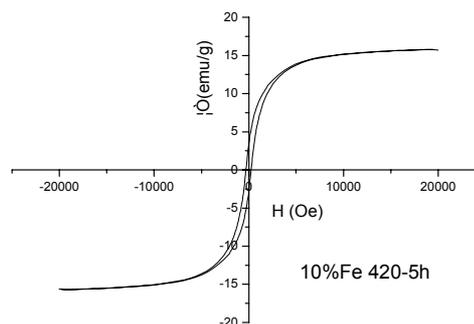


Fig.4 Magnetization curve of nano-iron/carbon composite prepared at 420□-5h in the presence of 10% ferrocene

Fig.1 TEM images of the nanosize iron particles/carbon