Self-Recurring Behavior of Nano-Metal Compound Particle -Porous Carbon Composite

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Introduction

Metal/porous carbon composites have interesting specialty, such as catalysts1) and absorbents2-3), an electrode of electric double layer capacitor4). These porous carbon composites with highly dispersed ultrafine metal compounds were prepared by carbothermal reduction from metal ion exchanged resin (MIER-CTR)5). We have found that metallic Ni or Fe/porous carbon composites by the MIER-CTR method have "self-recurring" behavior6,7), that is, the trace created by a quadrangular pyramid shaped diamond needle gradually disappeared within few minutes for the cases of metallic nickel and iron oxide/porous carbon composites. The photographic images of this phenomenon are shown in Fig.1.

In this work, the “self-recurring” phenomenon was examined in relation with the preparation conditions of the composite such as carbonization temperature, air treatment before carbonization, raw materials, metal content, etc.

Experimental

A commercial chelate resin (DIAION CR11, Mitsubishi Chemical, Japan) was used as a precursor of carbonized materials. Each of Ni2+, Fe2+ and Fe3+ was adsorbed into the resin by the conventional ion exchange procedure. The metal content of the carbonized material was controlled by the amount of metal ion adsorbed. After ion exchange, the resin was washed by distilled water and dried at room temperature.

An electric furnace was maintained at 120°C for 1 hour then temperature was raised to carbonization temperature (400~700°C) at a constant rate of 5°C/min, and held for 3 hours in a gas streams of N2 (300ml/min). In some cases, the resin was treated for 1 hour at 180~250°C in a gas streams of air (300ml/min) before carbonization.

Crystalline metal compounds in the composites were identified by the powder X-ray diffraction (XD-3A, Shimadzu). The metal content in the composite was evaluated by thermogravimetric method (TG30, Shimadzu). The specific surface area (SJ) was measured by the N2 BET method at 77K (BELSORP28SP, Nippon BEL Co. Ltd). The micro-

structure of the composites was observed by TEM (EM-002B, Topcon Pleasanton, CA). Microvickers hardness (Hv) was measured (MVK-G2, Akashi) 12 times for each sample (load:1~300g, 10 seconds).

Results and Discussion

The preparation conditions and physico-chemical properties of the Ni/C composites are shown in Table I. The microvickers hardness of some samples were not measured, because the needle trace disappeared after loading a diamond needle into the test sample. The needle trace faded out completely within 90 sec. This disappearance of the mark was observed when the needle load exceeded 25g. The formation of metallic nickel particles in the composites was confirmed by XRD. The disappearance of the needle trace was observed for the samples (Table 1, No. 8, 10, 11, 14) prepared under the following conditions:

1) Carbonization temperature was below soot. When carbonization was done above 700°C, the disappearance was not seen (Fig. 2). Graphitic carbon was formed and the structure of carbon matrix changed.

2) The nickel content of the composite was more than 13.5wt% (See No.4-10) (Fig.3).

3) Heat treatment in air (at 200-220°C) before carbonization was necessary even though Ni content was more than 13.5 wt% (Fig.3).

The diameters of the crystalline compounds and specific surface area (Sg) of the composites are also shown in the Table I. These do not have any direct relationship with the disappearance of needle trace.

The comparisons of the TEM images of the Ni/C composites are shown in Figs. 4 (No.10) and 5 (No. 5). The diameter of the metallic nickel particle was about 10 nm in the composite of No.10, which showed the “self-recurring” phenomenon. However, when the particle diameter of nickel was distributed in the range of 10 - 60 nm (No.5), the disappearance phenomenon was not observed. These results indicate that the microstructure of the metal-porous carbon composite correlates closely to the phenomenon of the needle trace disappearance.
The Fe/carbon (Fe/C) composite showed the similar results to those of Ni/C. The preparation conditions of the composites, for which the disappearance phenomenon were observed, were almost the same as the Ni/C. In Fe/C, metal components identified by XRD were FeO and Fe3O4. When FeO was produced in the composite, the needle trace did not fade out. Although the Fe/C composites containe particles with large diameter, the needle trace disappeared.

**Conclusion**

The “self-recurring” phenomenon was observed for the Ni/carbon composite prepared by the metal ion-exchange resin. The preparation condition for the “self-recurring” phenomenon were as follows:

1) Carbonization temperature was below 500°C
2) Preoxidation in air at 200 ~ 220°C in air before carbonization was applied.
3) The Ni content of the composite was more than 13.5wt%.

The composite of both carbon structure and metal component are responsible for the needle trace disappearance phenomenon.

**References**

6. Y. Sakata, A. Muto, M. A. Uddin, M. Tanihara, K. Harino, J. Takada, and Y. Kusano, Preparation of porous carbon composite with highly dispersed ultra fine metal compound from metal ion exchange resin. —Hardness and magnetic properties —, *J. Japan Soc. of particle and pow-
Fig. 1 Photographs of the “Self-Curring” phenomenon.
Table I Preparation conditions & physico-chemical properties of Ni/C composite

<table>
<thead>
<tr>
<th>No.</th>
<th>Precursor</th>
<th>Heating Temp [°C](1)</th>
<th>Carbonization Temp [°C](2)</th>
<th>Hv(3)</th>
<th>Ni Content</th>
<th>XRD(4)</th>
<th>Crystalline Diameter [nm](5)</th>
<th>Yield(6)</th>
<th>Sg [m(^2)/g-Carbon]</th>
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<tr>
<td>1</td>
<td>CR11-Ni(^{2+})</td>
<td>none</td>
<td>400</td>
<td>95</td>
<td>0.257</td>
<td>Ni</td>
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<td>0.31</td>
<td>210</td>
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<td>2</td>
<td>CR11-Ni(^{2+})</td>
<td>200(N(_2))</td>
<td>400</td>
<td>71</td>
<td>0.204</td>
<td>Ni</td>
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<td>3</td>
<td>CR11-Ni(^{2+})</td>
<td>180(Air)</td>
<td>400</td>
<td>60</td>
<td>0.215</td>
<td>Ni</td>
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<td>0.29</td>
<td>100</td>
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<td>4</td>
<td>CR11-H(^{+})</td>
<td>200(Air)</td>
<td>400</td>
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<td>-</td>
<td>no peak</td>
<td>-</td>
<td>0.30</td>
<td>270</td>
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<td>200(Air)</td>
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<td>30</td>
<td>0.068</td>
<td>no peak</td>
<td>-</td>
<td>0.22</td>
<td>310</td>
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<td>200(Air)</td>
<td>400</td>
<td>53</td>
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<td>no peak</td>
<td>-</td>
<td>0.19</td>
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<td>-</td>
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<td>350</td>
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<td>0.135</td>
<td>Ni</td>
<td>24</td>
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<td>340</td>
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<td>Ni</td>
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<td>Ni</td>
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<tr>
<td>14</td>
<td>CR11-Ni(^{2+})</td>
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<td>Ni</td>
<td>38</td>
<td>0.14</td>
<td>470</td>
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<td>Ni, Gr</td>
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<td>Ni, Gr</td>
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<td>0.20</td>
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</table>

1) Heat Treatment with 5°C/min. to heating temperature and hold for 1h in a stream of Air or N\(_2\).
2) Heat Treatment with 5°C/min. to carbonization temperature and hold for 3h in a stream of N\(_2\).
3) O means concavity disappear. Load: 100g for 10seconds.
4) Metal compound identified by XRD analysis. Gr: graphite
5) Calculated by the Scherrer’s equation (parameter K=1).
6) g/composite/g-dry resin

Fig. 2 The effect of carbonization temperature on “self-recurring” phenomenon.
Fig. 3 The effect of Ni content on the “self-recurring” phenomenon.
Fig. 3 The effect of Ni content on the “self-recurring” phenomenon

Fig. 4 TEM image of Ni/carbon composite (Table 1, No.5)

Fig. 5 TEM image of Ni/carbon composite (Table 1, No. 10)