

Elastic behavior of metal compound / microporous carbon composite

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Metal / microporous carbon composites were prepared by carbothermal reduction of metal ion-exchanged resin (MIER-CTR). The particles of the metal compounds were in nanometer sizes and highly dispersed in the porous carbon matrix. After microvickers hardness measurement of the composites, the pyramid-indentation in some samples disappeared reversibly. This phenomenon happened within 90 sec as the indentation load was removed. In this work, both the preparation conditions and microstructure of the composite were examined to clarify the cause of this curious phenomenon.

Key words: elasticity, nano-particle, microporous carbon, composite, metal

1. Introduction

Metal / porous carbon composites have been used as catalysts¹⁾ and absorbents^{2,3)}. Porous carbon composites with highly dispersed ultrafine metal compounds were prepared by carbothermal reduction from metal ion exchanged resin (MIER-CTR)⁴⁾. Metal compounds having high hardness such as tungsten carbide or tungsten nitride were prepared in the porous carbon matrix by this method. Microvickers hardness (Hv) of the composites was measured. It was found that the needle 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.

In this work, the phenomenon that is the disappearance of the needle trace after the hardness measurement, was examined from in relation with the

preparation conditions of the composite such as carbonization temperature, air treatment before carbonization, raw materials, metal content, etc. The correlation between the needle trace disappearance and the microstructure of the metal / metal compound particles in the composites was discussed.

2. Experimental Procedure

A commercial chelate resin (DIAION CR11, Mitsubishi chemical) 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 thermogravimetry method (TG30, Shimadzu). The specific surface area (S_g) was measured by the N₂ BET method at 77K (BELSORP28SP, Nippon BEL Co. Ltd). The microstructure 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).

3. 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 photographic images of this phenomenon are shown in Fig.1. The needle trace faded out completely within 90 sec. This disappearance of the mark was observed when the needle load exceeded 25g. The detail of dynamic behavior (such as disappearance time) will be reported elsewhere. 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 I, No. 8, 10, 11, 14) prepared under the following conditions: 1) Carbonization temperature was below 500°C. (When carbonization was done above 700°C, the disappearance was not

seen.) 2) Heat treatment (200-220°C) before carbonization was applied. 3) The nickel content of the composite was more than 13.5wt% (See No. 4-10). The diameters of the crystalline compounds and specific surface area, S_g 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. 2 (No. 10) and 3 (No. 5). The diameter of the metallic nickel particle was about 10nm in the composite of No. 10, which showed the disappearance phenomenon. When the particle diameter of nickel was distributed in the range of 10 - 60 nm (No. 5), however 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 the Ni/C. The preparation conditions and properties of the Fe/C composites are shown in Table II. The preparation conditions of the composites, for which the disappearance phenomenon were observed, were almost the same as the Ni/C. In the 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 contain Fe₃O₄ particles with large diameter (No. 3-6, 9-12, in Table II), the needle mark disappeared. This result suggests that the composite of both the structure and metal component are responsible for the needle trace disappearance phenomenon.

Table I Preparation parameters & physico-chemical properties of Ni/C composite

No.	Precursor	Heating Temp. [°C] ¹⁾	Carbonization Temp. [°C] ²⁾	Yield	XRD ³⁾	Crystalline diameter [nm] ⁴⁾	Ni Content [g-Ni/g-Composite]	Concavity behavior ⁵⁾	Hv [kgf/mm ²]	True Density [g/cc]	Sg [m ² /g-C]
1	CR11-Ni ²⁺	none	400	0.31	Ni	9.5	0.257	×	95	1.80	210
2	CR11-Ni ²⁺	200(N ₂)	400	0.30	Ni	6.4	0.204	×	71	1.60	150
3	CR11-Ni ²⁺	180(Air)	400	0.29	Ni	12	0.215	×	60	1.56	100
4	CR11-H ⁺	200(Air)	400	0.30	no peak	-	-	×	31	1.27	270
5	CR11-Ni ²⁺	200(Air)	400	0.22	no peak	-	0.068	×	30	1.46	310
6	CR11-Ni ²⁺	200(Air)	400	0.19	no peak	-	0.093	×	53	1.37	340
7	CR11-Ni ²⁺	200(Air)	400	0.20	no peak	-	0.120	×	30	1.25	350
8	CR11-Ni ²⁺	200(Air)	400	0.26	Ni	24	0.135	○	28	1.37	340
9	CR11-Ni ²⁺	200(Air)	400	0.18	Ni	32	0.157	○	26	1.45	420
10	CR11-Ni ²⁺	200(Air)	400	0.20	Ni	32	0.258	○	31	1.68	460
11	CR11-Ni ²⁺	220(Air)	400	0.17	Ni	32	0.288	○	29	1.81	450
12	CR11-Ni ²⁺	250(Air)	400	0.12	Ni	32	0.380	×	28	2.17	390
13	CR11-Ni ²⁺	none	500	0.30	Ni	11	0.258	×	178	1.95	390
14	CR11-Ni ²⁺	200(Air)	500	0.14	Ni	38	0.388	○	62	2.19	470
15	CR11-Ni ²⁺	none	700	0.29	Ni,Gr	48	0.283	×	82	2.64	120
16	CR11-Ni ²⁺	200(Air)	700	0.20	Ni,Gr	48,15	0.250	×	63	2.59	430

1)Heat Treatment with 5°C/min. to heating temperature and hold for 1h in a stream of Air or N₂.

2)Heat Treatment with 5°C/min. to carbonization temperature and hold for 3h in a stream of N₂.

3)Metal compound identified by XRD analysis. Gr: graphite

4)Calculated by the Scherrer's equation (parameter K=1).

5)○ means concavity disappear. Load: 100g for 10seconds.

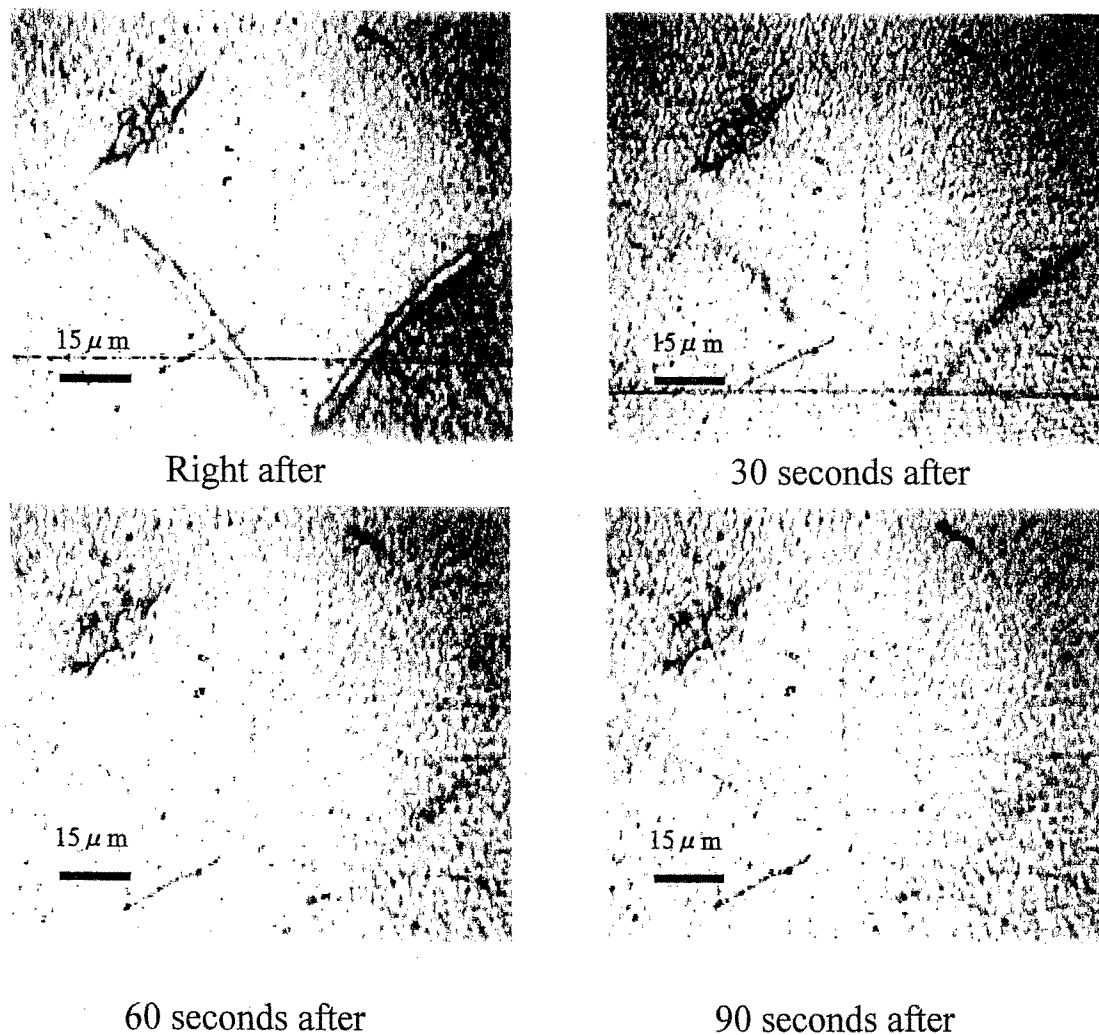


Fig. 1 The needle trace disappearance phenomenon of Ni/C composite (Table I, No. 10)*
Load 100g, 10 seconds

*These photographs are showing the measurement of microvickers hardness. The concavity created by quadrangular pyramid shape diamond needle gradually disappeared with the lapse of time.

Table II Preparation parameters & physico-chemical properties of Fe/C composite

No.	Precursor	Heating Temp. [°C] ¹⁾	Carbonization Temp. [°C] ²⁾	Yield	XRD ³⁾	Crystalline diameter [nm] ⁴⁾	Fe Content [g-Fe/g-Composite]	Concavity behavior ⁵⁾	Hv [kgf/mm ²]	True Density [g/cc]	S _g [m ² /g-C]
1	CR11-Fe ²⁺	none	400	0.30	FeO	19	0.230	×	79	1.68	~0
2	CR11-Fe ²⁺	200(N ₂)	400	0.24	FeO	19	0.252	×	60	1.60	~0
3	CR11-Fe ²⁺	180(Air)	400	0.16	Fe ₃ O ₄	31	0.434	○	36	2.27	420
4	CR11-Fe ²⁺	200(Air)	400	0.16	Fe ₃ O ₄	31	0.512	○	32	2.31	290
5	CR11-Fe ²⁺	220(Air)	400	0.16	Fe ₃ O ₄	31	0.435	○	26	2.34	390
6	CR11-Fe ²⁺	200(Air)	500	0.13	Fe ₃ O ₄	46	0.539	○	66	3.29	350
7	CR11-Fe ³⁺	none	400	0.34	FeO	24	0.224	×	53	1.56	60
8	CR11-Fe ³⁺	200(N ₂)	400	0.35	FeO	24	0.234	×	69	1.58	~0
9	CR11-Fe ³⁺	180(Air)	400	0.29	Fe ₃ O ₄	31	0.216	○	25	1.66	580
10	CR11-Fe ³⁺	200(Air)	400	0.36	Fe ₃ O ₄	31	0.196	○	23	1.76	500
11	CR11-Fe ³⁺	220(Air)	400	0.23	Fe ₃ O ₄	31	0.203	○	31	1.99	500
12	CR11-Fe ³⁺	200(Air)	500	0.27	Fe ₃ O ₄	37	0.239	○	67	1.96	530

1) Heat Treatment with 5°C/min. to heating temperature and hold for 1h in a stream of Air or N₂.

2) Heat Treatment with 5°C/min. to carbonization temperature and hold for 3h in a stream of N₂.

3) Metal compound identified by XRD analysis.

4) Calculated by the Scherrer's equation (parameter K=1).

5) ○ means concavity disappear. Load: 100g for 10seconds.

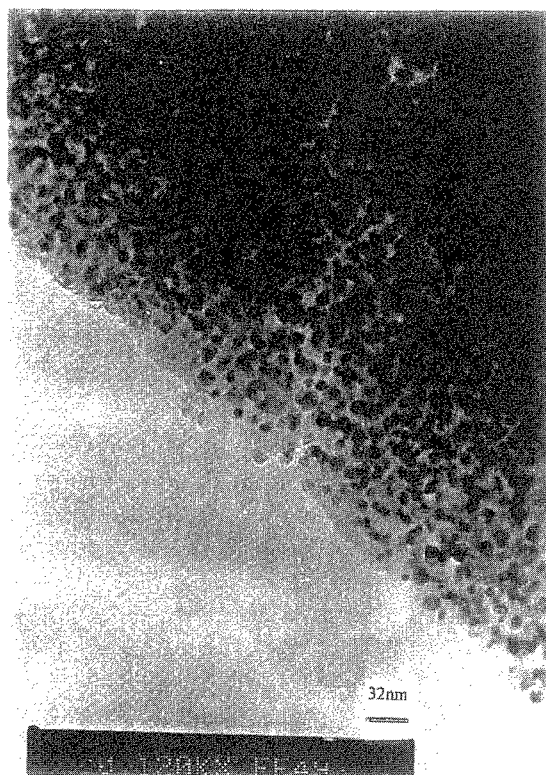


Fig. 2 TEM image of Ni/C composite (Table I, No.10)

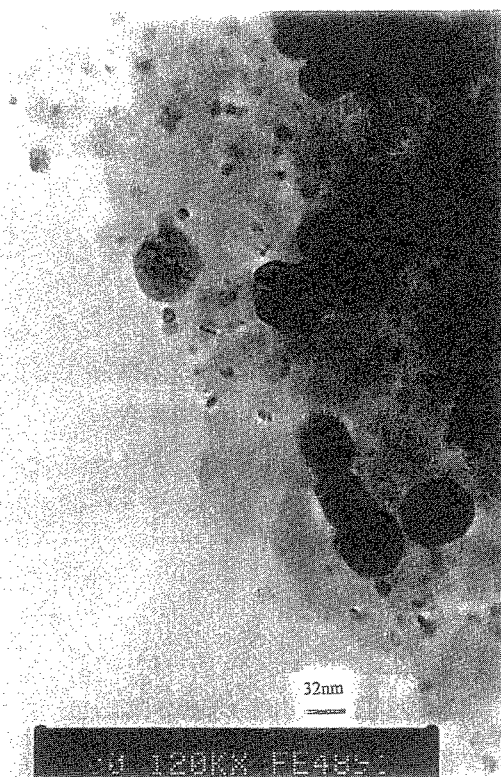


Fig. 3 TEM image of Ni/C composite (Table I, No.5)

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