

DESIGNING OF THE MECHANICALLY PREPARED NANOSTRUCTURED GRAPHITE AS HYDROGEN STORAGE MEDIA

S. Orimo¹, T. Matsushima¹, H. Fujii¹, T. Fukunaga², G. Majer³

¹Faculty of Integr. Arts and Sciences, Hiroshima University, Higashi-Hiroshima 739-8521, Japan

²Research Reactor Institute, Kyoto University, Osaka 590-0494, Japan

³Max-Planck-Institut für Metallforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany

Introduction

Much attention has been recently paid to the investigations of the hydriding properties of carbon-related materials with specific nanometer-scale structures [1]. In our previous paper [2], we have reported fundamental information about the structures and hydrogen concentrations in the nanostructured graphite prepared by mechanical milling under hydrogen atmosphere. After the expansion of the graphite interlayer, the long-range ordering of the interlayer disappears continuously with increasing milling time. The hydrogen concentration, precisely determined by the oxygen combustion analysis, reaches up to 7.4 mass% (CH_{0.95}) after milling for 80 h, as is shown in Fig. 1. Systematic result on neutron diffraction measurements of the samples will be reported by Fukunaga et al. [3].

The main purpose of present work is to clarify the thermal desorption (dehydriding) property of the nanostructured graphite by using the sample mechanically milled for 80 h [4].

Experimental

300 mg of high-purity graphite powder (99.997 % purity, ~200 μm) as a host sample was mechanically milled by using the planetary ball mill apparatus (Fritsch P7) under high-purity hydrogen (99.99999 % purity) or deuterium (99.99 % purity) of 1.0 MPa as an initial pressure for 80 h. The sample before and after the milling was handled in the glove-box filled with purified argon, so as to minimize oxidation and water-adsorption.

The sample thus prepared were examined by thermal desorption *mass*-spectroscopy (TDS, ANELVA M-QA 200TS), specially set up in the glove-box.

Results and discussion

In Fig. 2(a), there are two desorption peaks with *mass*-

number = 2, starting from *ca.* 600 K and 950 K, respectively. These desorption phenomena are reproducible also in the sample mechanically milled under deuterium atmosphere, as shown Fig. 2(b). Therefore, the results shown in Fig. 2(a) are surely coming, not from adsorbed water or so, but from the hydrogen inside the nanostructured graphite. A small amount of the desorption peaks corresponding to the hydrocarbons, with *mass*-number = 16 from CH₄ and 28 from C₂H₆, respectively, is also detected around the first desorption peak in Fig. 2(a).

The first desorption peak in Fig. 2(a) might have, in our opinion, similar origin to the main desorption peaks of hydrogen from the single-walled carbon nanotubes which have been recently reported by Dillon et al. [5] and Hirscher et al. [6]. Here the apparent desorption temperatures tend to be modified by “kinetics” effects, depending on amounts of metallic impurities and heating rates, or so. In addition, hydrogen desorption from amorphous-carbon films, so called diamond-like carbons, with CH₂ and/or CH₃ coordinations has been detected [7-9] at similar temperatures to the first desorption peak in Fig. 2(a). Partial formation of CH₃ coordination with *sp*³ bond originated from the defective structures of the nanostructured graphite is also suggested by the increase of background around 1525 cm⁻¹ in the Raman spectroscopy [4].

References

1. Züttel A, Nützenadel Ch, Sudan P, Mauron Ph, Emmenegger Ch, Rentsch S, Schlapbach L, Weidenkaff A, Kiyobayashi T. Hydrogen sorption by carbon nanotubes and other carbon nanostructures. *J. Alloys Comp*, in press.
2. Orimo S, Majer G, Fukunaga T, Züttel A, Schlapbach L, Fujii H. Hydrogen in the mechanically prepared nanostructured graphite. *Appl. Phys. Lett.* 1999; 75(20):3093-3095.

3. Fukunaga T, Itoh K, Orimo S, Fujii H, to be submitted in Acta mater..
4. Orimo S, Matsushima T, Fujii H, Fukunaga T, Majer G. Defective carbon for hydrogen storage -thermal desorption property of the mechanically prepared nanostructured graphite-. submitted to J. Appl. Phys..
5. Dillon AC, Gennett T, Alleman JL, Jones KM, Parilla PA, Heben MJ. Proceedings of the 2000 DOE/NREL Hydrogen Program Review, May 8-10 (2000).
6. Hirscher M, Becher M, Haluska M, Quintel A, Skakalova V, Choi YM, Dettlaff-Weglikowska U, Roth S, Stepanek I, Bernier P, Loenhardt A, Fink J. Hydrogen storage in carbon nanostructures. J. Alloys Comp, in press.
7. Nyaiesh AR, Nowak WB. Chemisorped hydrogen on α -carbon films. J. Vac. Sci. Technol. A 1983;1(2):308-312.

8. Fink J, Müller-Heinzerling Th, Pflüger J, Scheerer B, Dischler B, Koidl P, Bubenzer A, Sah RE. Investigation of hydrocarbon-plasma-generated carbon films by electron-energy-loss spectroscopy. Phys. Rev. B 1984; 30(8):4713-4718.
9. Gonzalez-Hernandez J, Chao BS, Pawlik DA, J. Vac. Sci. Technol. A 1989;7(3):2332-2338.

Acknowledgements

This work was financially supported by the New Energy and Industrial Technology Development Organization (NEDO), "Industrial Technology Research Grant Program in 2000", by the Ministry of Education, Science, Sports and Culture, "Grant-in-Aid for Scientific Research on Priority Areas", and by the Deutsche Forschungsgemeinschaft (DFG).

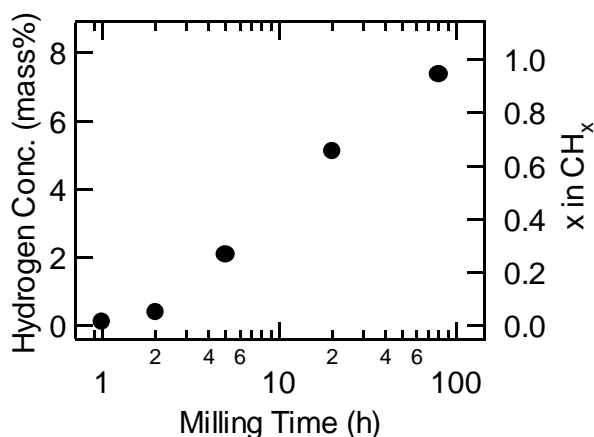


Figure 1.

Total hydrogen concentration in the nanostructured graphite, as a function of milling time under hydrogen atmosphere [2].

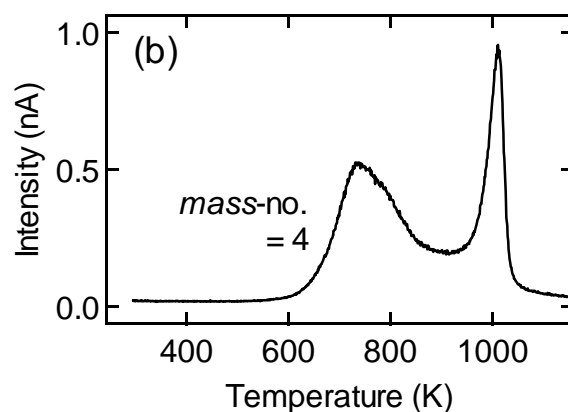
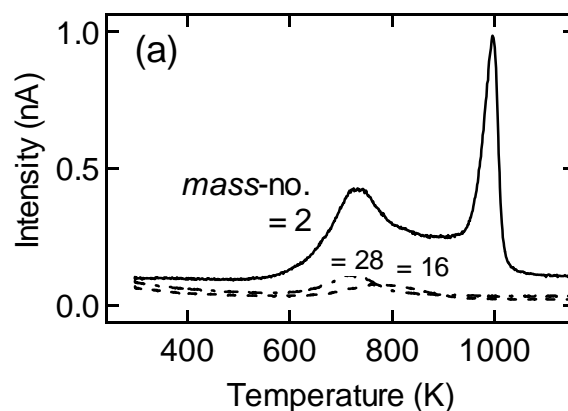


Figure 2.

Thermal desorption *mass*-spectroscopy (TDS) of the nanostructured graphite mechanically milled under hydrogen (a) and deuterium (b) atmospheres, respectively [4].