

HYDROGEN STORAGE PROPERTIES ON MECHANICALLY MILLED GRAPHITE

T. Ichikawa^{*1,3}, D.M. Chen², S. Isobe³, E. Gomibuchi³, H. Fujii^{1,3}

¹*Natural Science Center for Basic Research and Development, Hiroshima University,
Higashi-Hiroshima 739-8526, Japan*

²*Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110015, China*

³*Graduate School of Advanced Sciences of Matter, Hiroshima University,
Higashi-Hiroshima 739-8530, Japan*

Abstract

We investigated hydrogen absorption/desorption and structural properties in mechanically milled graphite under hydrogen pressures up to 6 MPa to clarify catalytic and hydrogen pressure effects in the milling. The results indicate that a small amount of iron contamination during milling plays a quite important role as a catalyst for hydrogen

* Corresponding Author: T. Ichikawa, Address: 1-7-1 Kagamiyama, Higashi-Hiroshima 739-8521, Japan, E-mail: tichi@hiroshima-u.ac.jp, Fax: +81-824-24-0757

absorption/desorption properties in graphite. Two-peak structure for hydrogen desorption in the TDS profile is due to existence of two different occupation sites for hydrogen, which is caused by the existence of high dispersing iron on graphite. From the experiment of high pressure milling, we clarified that the number of defects in graphite decreases with increasing the atmospheric hydrogen pressure during milling, leading to the decrease in the absorbed hydrogen content and the stabilization of hydrogen on the occupation sites. In addition, we confirmed the existence of physisorption-like reversible hydrogen at room temperature in the graphite prepared by milling under high pressure hydrogen atmosphere above 3 MPa. This unstable hydrogen might strongly be correlated with the existence of the lamella structure in nanometer scale, which only leaves in graphite prepared by high pressure milling.

Keywords: Hydrogen, Graphite, Catalysis, Chemisorption, Iron, Carbides

1. Introduction

Since Dillon *et al.*[1] reported the hydrogen storage properties of the carbon nanotube, which couldn't be confirmed by anyone else unfortunately, the hydrogenating behaviors of carbon-related nano-structural materials have been extensively investigated. However, no unified opinion has been established for the ability of hydrogen sorption in the carbon related materials, because many reports on the amount of hydrogen absorption and desorption scattered too widely, ranging from ~0 wt.% to 67 wt.% [1 - 4].

In our previous research, we reported that the chemisorbed hydrogen concentration reaches up to about 7 wt.% in the nano-structural graphite prepared by mechanically milling under 1 MPa hydrogen atmosphere with a planetary ball mill equipment [5,6,7]. We deduced that one-fifth of the chemisorbed hydrogen forms C-H covalent bonds along the edges of the graphene sheets and the rest is trapped at graphite inter-layered defective sites. However, we didn't know why and how such hydrogen absorbing/desorbing sites could be produced in the graphite during mechanically milling under hydrogen atmosphere. In this paper, we report the more important factor for hydrogenation of graphite prepared by mechanical milling from the viewpoints of basic research and development on hydrogen storage.

2. Experimental details

2.1 Planetary Mill Equipment

As one of the methods for sample preparations, a planetary ball mill equipment (Fritch P7) was used in this work. In the milling process, total amount 300 mg of the powders and 20 (15) pieces of steel (ZrO_2) balls with diameter of 7.0 (10) mm were set into the Cr steel (ZrO_2) vessel, and milled with 400 rpm for 32 or 80 h under hydrogen gas pressure of 1.0 (0.9) MPa at room temperature. In this work, high-purity graphite powder (Goodfellow, 99.997% in purity, $\sim 200\mu m$ in diameter) and activated carbon (Kansai Coke and Chemicals Co. Ltd., Maxsorb) were milled for 80 h using steel vessel and balls, and other 6 kinds of samples were also prepared using the planetary type equipment for clarifying catalytic effects of iron. We used steel vessel and balls for milling the samples a, b, d and e, and ZrO_2 vessel and balls for milling the sample c and f. The milling time of samples a ~ c and

samples d ~ f are 80 h and 32 h, respectively. The sample b was washed on the sample a using an acid hot water for the purpose of taking off the iron, which came from steel vessel and balls during milling. The sample e was prepared by mechanical milling the mixture of the 1 at.% of Fe powder with a diameter of 20 nanometer on average (purchased from Shinku-Yakin) and graphite.

2.2 Vibrating Mill Equipment

For the purpose of clarifying hydrogen gas pressure effect during milling on hydrogen absorption and structural properties, we prepared some graphite using vibrating mill equipment under hydrogen pressures up to 6 MPa, in which a pressure gauge up to 6 MPa and reservoir with a well-known volume are equipped. The amount of 300 mg of high-purity graphite powder (Goodfellow) and 20 steel balls of 7 mm in diameter were put in the milling vessel made of Cr steel as well. First, the entire system composed of milling vessel, reservoir cell, pressure gauge and a few valves was degassed for 12 h below 1×10^{-4} Pa using a turbo-molecular pump set. Then, hydrogen gas of 0.3, 1.0, 3.0 and 6.0 MPa, respectively, was introduced and then the graphite was milled for 80 h. Prior to the evaluation of physisorption-like unstable hydrogen concentration at room temperature, high-purity hydrogen gas (99.9999% purity) of 6.000 MPa was exactly filled in the milling vessel with graphite before and after milling, and kept for 6 h at $25.0 \pm 0.1^\circ\text{C}$. Then, the valve connecting the milling vessel and the reservoir cell was closed, and only the reservoir cell was degassed below 3×10^{-4} Pa. Finally, after the valve was opened, the equilibrium pressures in the system with the mechanically milled graphite for 80 h under hydrogen pressures of 0.3, 1.0, 3.0, 6.0 MPa were determined, which is shown in Table 1. Here, the

blank pressure was defined as an equilibrium pressure in the system before milling. Thus, the physisorption-like hydrogen concentration was estimated from the difference between the blank pressure before milling and equilibrium pressures after milling.

2.3 Sample Analyses

All the samples were handled in a glove box (Miwa Industries) filled with purified argon to minimize oxidation and water adsorption. The as-prepared samples were characterized by X-ray diffraction measurement (XRD, RINT-2100 RIGAKU, $\text{CuK}\alpha$ radiation) and thermal desorption mass-spectroscopy (TDS, ANELVA M-QA200TS). Here, TDS equipment was especially designed and built up for using it in the glove box filled with purified argon, which permitted measurement of TDS without exposing the samples to air at all. In the thermal analysis measurement, high-purity helium (purity > 99.9999%) was adopted as a carrier gas, and the heating rate was 10 °C/min. The hydrogen storage capacity was determined by oxygen-combustion hydrogen analysis (OCHA, Perkin Elmer 2400 α CHN).

3. Results and discussions

3.1 Structure of Initial Materials

Figure 1 shows the TDS profiles for hydrogen gas from the samples made of graphite and activated carbon by planetary milling apparatus for 80 h under hydrogen of 1.0MPa for starting pressure. We can see two-peak structure in both the TDS profiles, which is due to existence of two different occupation sites for hydrogen. This indicates that the initial structure of the materials has no relation to the hydrogenating and dehydrogenating properties, and the nano-structured activated carbon has the same sites and basal structure

unit in micro-scope scale as nano-structured graphite after milling for 80h under hydrogen.

3.2 Catalytic Effect of Iron Contamination

Figure 2 shows the XRD profiles of mechanically milled graphite by planetary type machine after annealing at 25 (R.T.), 150, 300, 450 and 600 °C under high vacuum for 8 h. The iron carbide, Fe₃C crystalline grows up from 300 °C, where the iron contained in Fe₃C comes from steel vessel and balls during milling. We confirmed that hydrogen is desorbed from low temperature first peak around 300 °C, where the crystalline growth of Fe₃C set up. This indicates that Fe₃C plays a quite important role as a catalyst for hydrogen release from graphite. We also confirmed that the (002) diffraction peak of graphite recovers after heat treatment at 600 °C.

TDS profiles of the 6 kinds of samples a ~ f are shown in Figure 3. We can easily notice that the two-peak structure appears only in the samples containing a considerable amount of iron, that is, in Fig. 3a and 3e, where the sample e is prepared by artificially added a small amount of iron nano-powder into initial graphite before the milling treatment. The sample d shows very weak two-peak structure as shown in Fig. 3d, because the sample is contaminated with a very small amount of iron during milling for 32 h from the steel vessel and balls. On the other hand, there is no two-peak structure in the samples without containing iron as is seen in Fig. 3b, 3c and 3e. Therefore, we can conclude that the characteristic two-peak structure of hydrogen desorption from some hydriding graphite originates with the existence of the iron contamination during milling from steel vessel and balls.

3.3 Hydrogen Pressure Effect during Milling on Nano-structured Graphite

In Figure 4, TDS profiles for mass number of 2 (H_2 -gas) are shown for the nano-structured graphite milled for 80 h under various hydrogen pressures prepared by the vibrating milling method and under 1.0 MPa hydrogen pressure by planetary mill as well. We can see two-peak structure in all the TDS profiles. In our previous research, we have assigned the low temperature peak to the desorption of hydrogen atoms trapped at some defects between the graphite planes, and the high temperature peak to that of those trapped at the edges of graphene sheets. It is to be noted that the low temperature first peak of the sample milled by vibrating mill is weaker than planetary mill.

As is evident from Fig. 4, the second peak of hydrogen desorption unexpectedly shifts to the higher temperature side with increasing the milling pressure. However, in the case of the same pressure at the beginning of milling, the second peak temperature in the rotating milling process is almost the same as in the vibrating one, independent of the milling type. To clarify the pressure effect during milling, we compared the XRD profiles of the samples milled for 2h under hydrogen atmosphere of 0.3, 1.0, 3.0 and 6.0 MPa in Figure 5. The intensity of the main (002) diffraction peak increases with increasing hydrogen pressure during milling. This means that it is hard to make the defects in the graphite under high pressure condition on mechanical milling. Actually, we could confirm that the hydrogen absorbing content analyzed by OCHA decreases with increasing the milling pressure. These results indicate that higher hydrogen pressure milling leads to the decrease in the absorbed hydrogen content and the stabilization of hydrogen on the occupation sites, which are strongly related with the number of defects in the nano-structured graphite.

3.4 Unstable Physisorption-like Hydrogen

In Table 1, the pressure value and the gas kind during milling process by vibrating mill and equilibrium hydrogen pressure are listed for clarifying the existence of unstable physisorbed hydrogen at room temperature. And the stable chemisorbed hydrogen concentrations estimated by OCHA are also appended to this list for comparison. From this list, we estimated the physisorption concentration in the nano-structured graphite, indicating that the hydrogen concentration increases with increasing hydrogen gas pressure during milling. Thus, we emphasize that the claimed physisorption value has no origin from the increase of the free volume of the milling vessel because the density of the milled graphite tends to decrease. Also, we deduced that this kind of adsorption is reversible at room temperature with extremely high reaction rate and the adsorption amount did not change after 3 adsorption and desorption cycles were examined. Therefore, this adsorption is of a typical physisorption. It is noteworthy that the higher pressure hydrogen atmosphere during milling process is favorable to the generation of the reversible physisorption site in the graphite.

In addition, we obtained the result that higher pressure hydrogen atmosphere during milling process suppresses the fracture rate of graphite and preserves the lamella structure within nanometer scale in the nano-structural graphite milled under higher hydrogen pressure. Therefore, considering the above results, it seems likely that the nanometer-scaled lamella structure in the milled graphite strongly correlates with the appearance of the physisorption-like hydrogen.

4. Conclusion

We examined the catalytic effect of Fe on (de-)hydrogenating and structural properties in

graphite prepared by mechanically milling under various hydrogen gas pressures.

We found the typical two-peak structure originated with the existence of the iron which highly dispersed in the nano-structured graphite during milling process. In addition, the first hydrogen desorption peak in the TDS profile starts to appear at the same temperature range as the Fe_3C crystalline grows up. We clarified that these results are due to the catalytic effect of nano-scaled iron contamination.

The structure transformation of the nano-structured graphite mechanically prepared under hydrogen atmosphere strongly depends on the hydrogen pressure. Higher pressure can suppress the fracture rate of the milled graphite more effectively. This is consistent with the result that the chemisorption concentration decreases with increasing the hydrogen pressure during milling. On the other hand, the physisorption hydrogen concentration in the graphite milled under high pressure hydrogen atmosphere reaches up to around 0.5 wt. % at room temperature. This physisorption hydrogen might originate in the typical lamella structure, which exists a lot in the nano-structural graphite under high pressure hydrogen atmosphere.

Acknowledgement

This work was financially supported in part by the Grant-Aid for Scientific Research on Kiban (B) and by the Grant-in-Aid for COE Research (No. 13CE2002) of the Ministry of Education, Science, Sports and Culture of Japan. The authors thank Dr. E. Ohta for the Oxygen Combustion measurement. They also thank Ms. N. Hanada, Mr. K. Tanabe, Dr. J.I. von Wild and Dr. S. Orimo for their help.

References

- [1] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, M.J. Heben, *Nature (London)* **386** (1997) 377.
- [2] H. Kajiura, S. Tsutsui, K. Kadono, M. Kakuta, M. Ata, Y. Murakami, *Appl. Phys. Lett.*, **82** (2003) 1105
- [3] A. Chambers, C. Park, R. Terry, K. Baker, N.M. Rodriguez, *J. Phys. Chem. B*, **102** (1998) 4253
- [4] A. Züttel, P. Sudan, Ph. Mauron, T. Kiyobayashi, Ch. Emmenegger, L. Schlapbach, *Int. J. Hydrog. Energy*, **27** (2002) 203
- [5] S. Orimo, G. Majer, T. Fukunaga, A. Züttel, L. Schlapbach, H. Fujii, *Appl. Phys. Lett.* **75** (1999) 3093.
- [6] S. Orimo, T. Matsushima, H. Fujii, T. Fukunaga, G. Majer, *J. Appl. Phys.* **90** (2001) 1545
- [7] T. Fukunaga, K. Itoh, S. Orimo, M. Aoki, H. Fujii, *J. Alloys Comp.* **327** (2001) 224

Figure 1. XRD profiles of the nanostructured graphite (upper) and activated carbon (lower) prepared by mechanical milling using planetary type milling apparatus.

Figure 2. XRD profiles of the nanostructural graphite milled by a planetary type milling method: as-milled sample without heat treatment (bottom) and samples heat-treated at 150, 300, 450 and 600 °C under a high vacuum condition below 3.0×10^{-4} Pa.

Figure 3. TDS profiles of the 6 kind samples; a: milled by steel vessel and balls for 80h, b: treated sample a with acid hot water, c: milled by ZrO₂ vessel and balls for 80h, d: milled by steel vessel and balls for 32h, e: mixture of graphite and small amount of iron milled by steel vessel and balls for 32h, f: milled by ZrO₂ vessel and balls for 32h.

Figure 4. TDS profiles of mass number 2 (H₂-gas) for the nanostructural graphite prepared by vibrating milling for 80 h under various hydrogen pressures; 0.3, 1.0, 3.0, 6.0 MPa and by planetary milling for 80 h under 1.0MPa.

Figure 5. XRD profiles of the nanostructural graphite milled for 2h by vibrating type mill equipment under various hydrogen pressure atmosphere.

Table 1. List of pressure value, the gas kind during milling process by vibrating mill, equilibrium hydrogen pressure, estimated unstable H₂ concentration and estimated stable H₂ concentration by OCHA (including the Ar case)

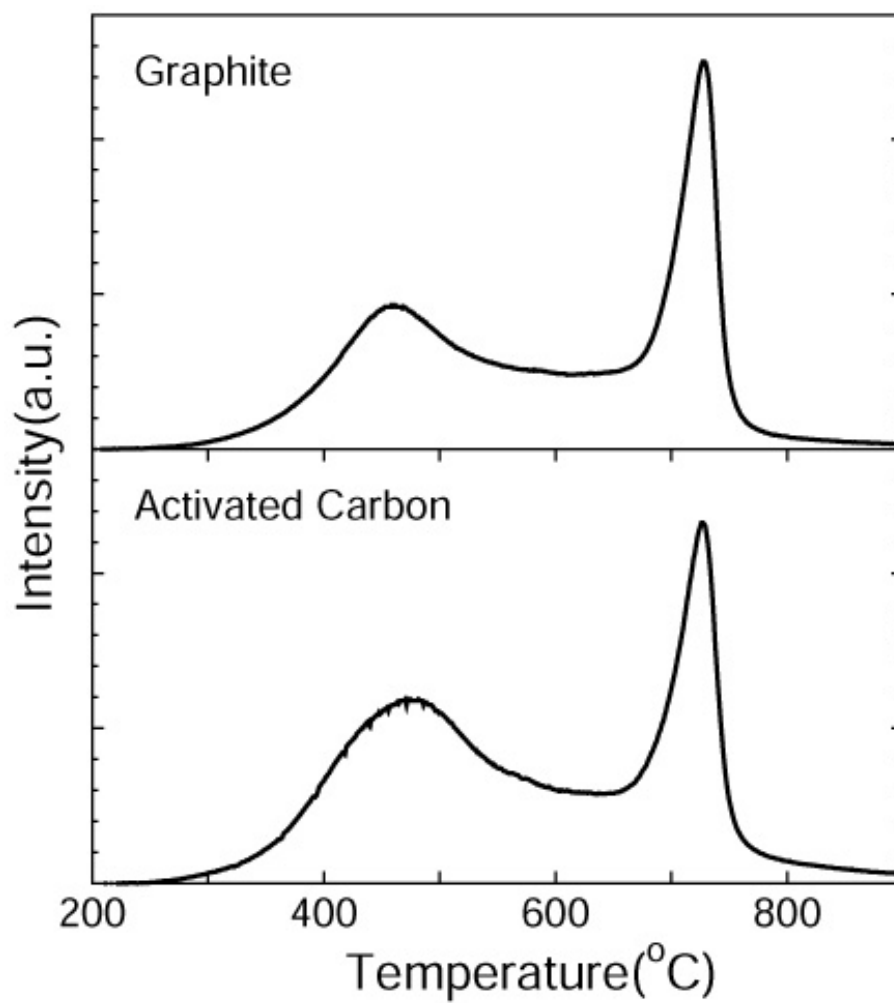


Figure 1. XRD profiles of the nanostructured graphite (upper) and activated carbon (lower) prepared by mechanical milling using planetary type milling apparatus.

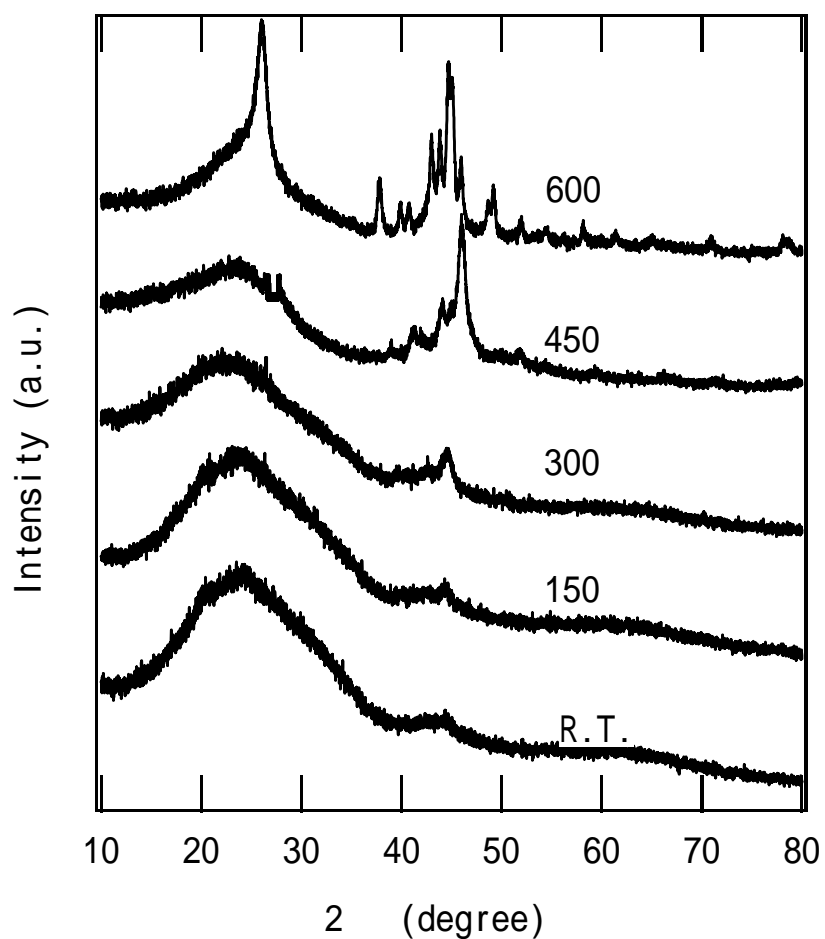


Figure 2. XRD profiles of the nanostructural graphite milled by a planetary type milling method: as milled sample without heat treatment (bottom) and samples heat-treated at 150, 300, 450 and 600 °C under a high vacuum condition below 3.0×10^{-4} Pa.

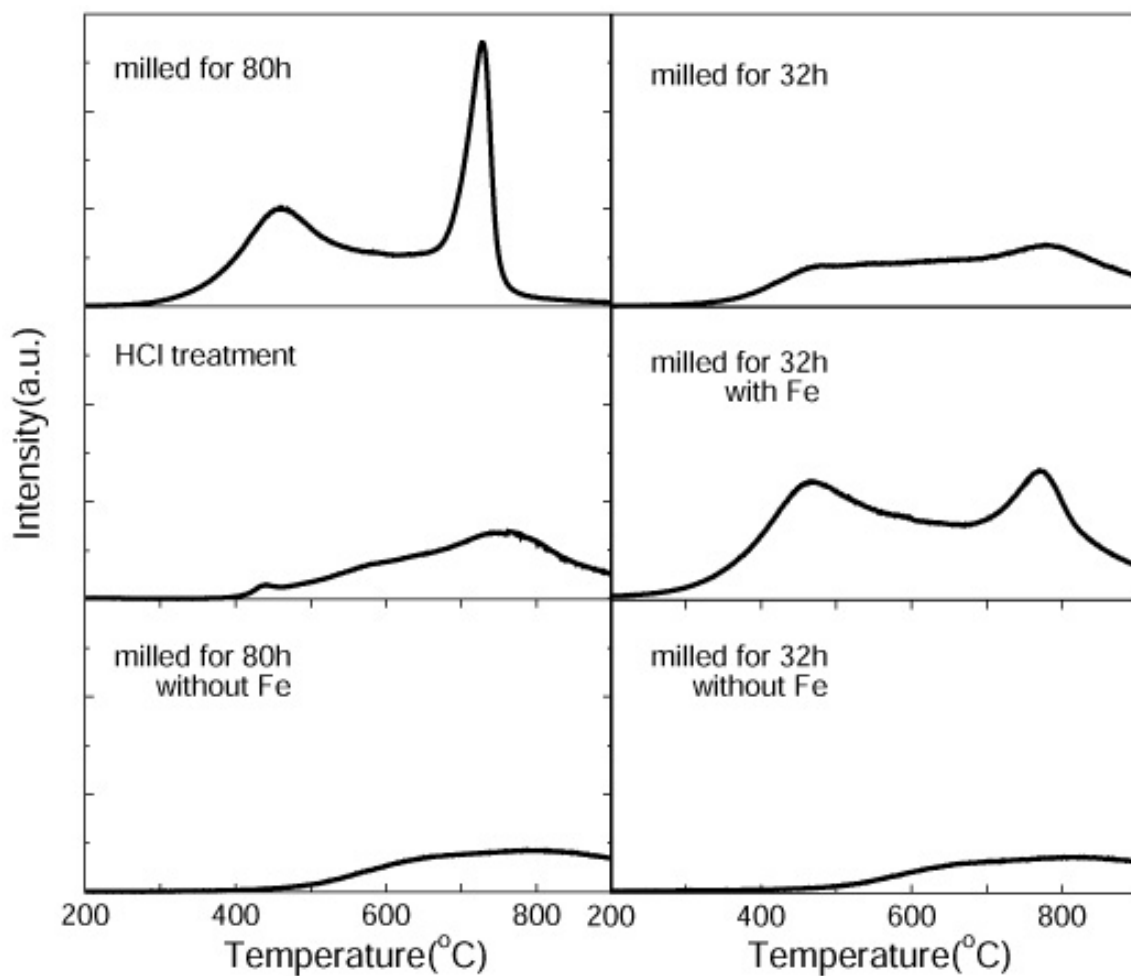


Figure 3. TDS profiles of the 6 kind samples; a: milled by steel vessel and balls for 80h, b: treated sample a with acid hot water, c: milled by ZrO_2 vessel and balls for 80h, d: milled by steel vessel and balls for 32h, e: mixture of graphite and small amount of iron milled by steel vessel and balls for 32h, f: milled by ZrO_2 vessel and balls for 32h.

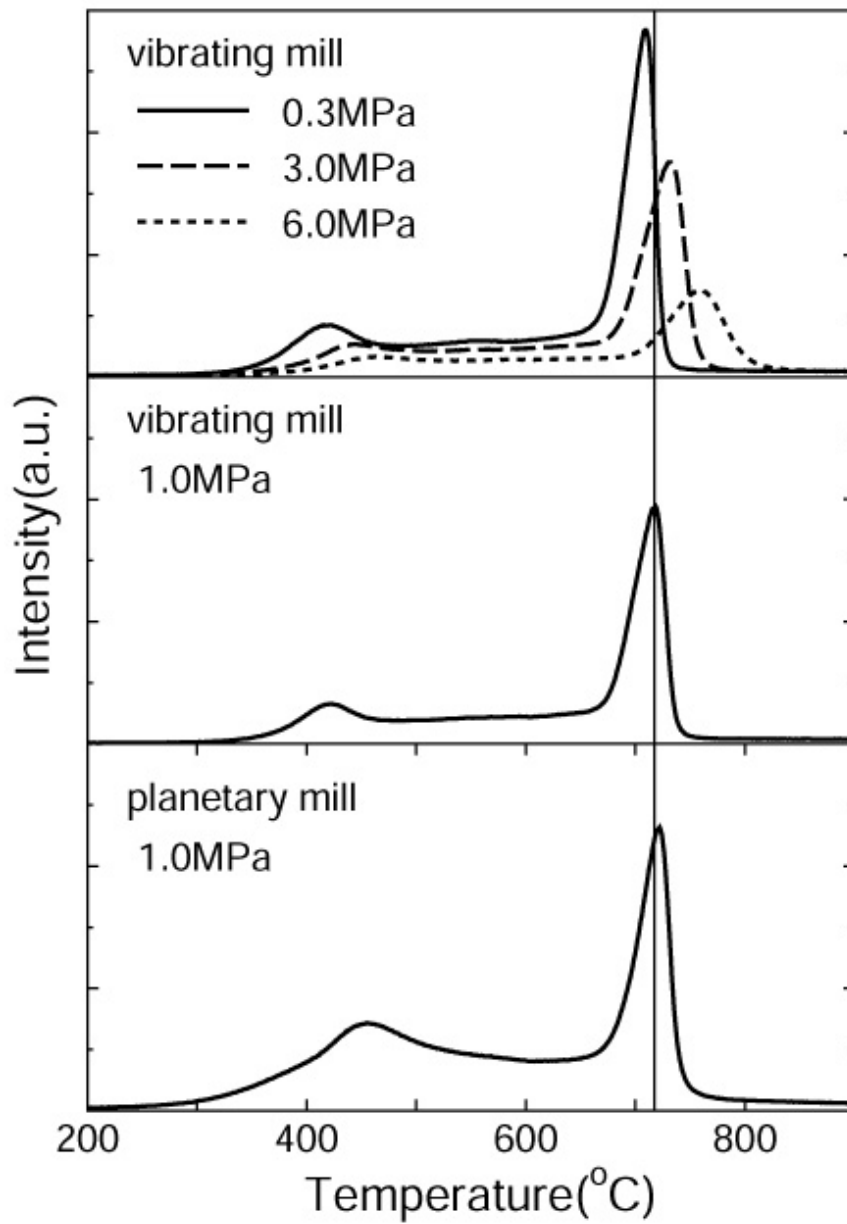


Figure 4. TDS profiles of mass number 2 (H_2 -gas) for the nanostructural graphite prepared by vibrating milling for 80 h under various hydrogen pressures; 0.3, 1.0, 3.0, 6.0 MPa and by planetary milling for 80 h under 1.0MPa.

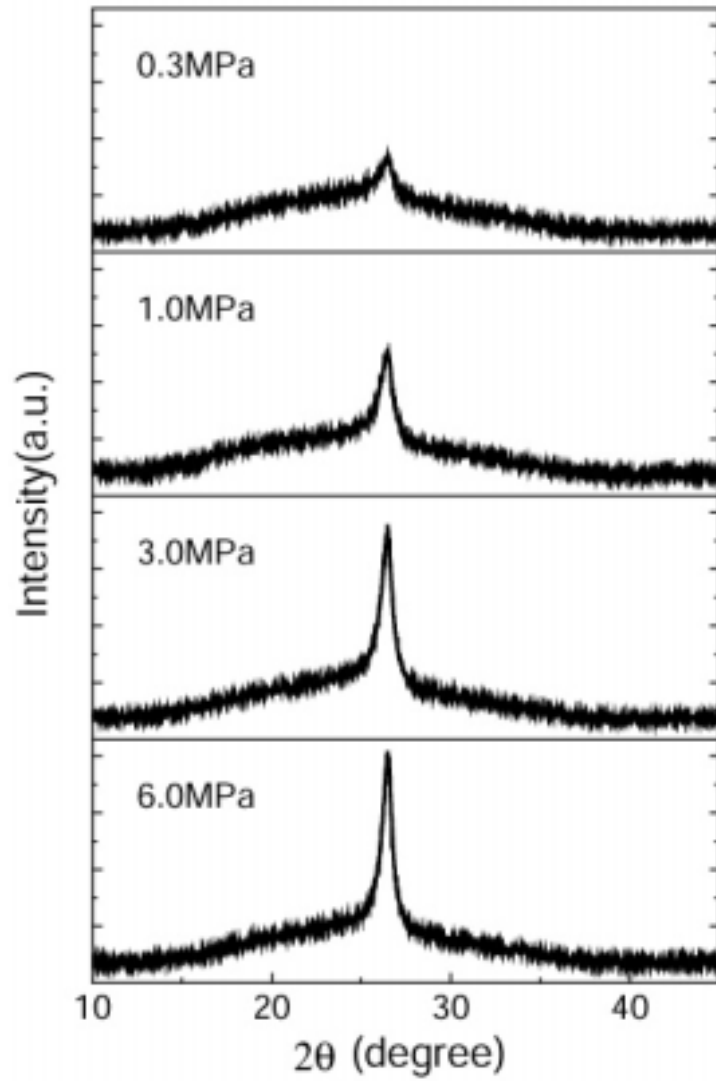


Figure 5. XRD profiles of the nanostructural graphite milled for 2h by vibrating type mill equipment under various hydrogen pressure atmosphere.

Pressure	Atmospheric Gas	Equilibrium H ₂ pressure	Concentration (unstable H ₂)	Concentration (stable H ₂)
Milling sample (after milling for 80 h)				
6.0MPa	H ₂	0.882MPa	> 0.5wt.%	6.1wt.%
6.0MPa	Ar	0.870MPa	~ 0.0wt.%	0.0wt.%
3.0MPa	H ₂	0.882MPa	~ 0.5wt.%	5.7wt.%
1.0MPa	H ₂	0.868MPa	~ 0.0wt.%	4.5wt.%
0.3MPa	H ₂	0.868MPa	~ 0.0wt.%	4.1wt.%
Host(before milling)				
		0.870MPa	0.0wt.%	0.0wt.%

Table 1. List of pressure value, the gas kind during milling process by vibrating mill, equilibrium hydrogen pressure, estimated unstable H₂ concentration and estimated stable H₂ concentration by OCHA (including the Ar case)