

Preparation of carbon from defluorination of PTFE supported by vapor deposition technique

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Introduction

Polytetrafluoroethylene(PTFE) is one of the most popular fluoropolymer which has a simple molecular chain structure of $-(CF_2-CF_2)_n-$. While this polymer is quite stable to most of chemicals, it is known to be reduced and corroded by alkali metals or their derivatives. During the defluorination of PTFE, it is considered that only carbon chain is remained to form sp^1 -bond carbon, that is, carbyne structure[1,2]. The carbyne is so active and unstable that it is easily cross-linked each other and usually changed to another carbon form with sp^2 -bond based structure soon. Hence, this technique using chemical defluorination of fluoropolymer has been often applied as a new route to obtain carbon material without pyrolysis of polymer, and some notable carbon materials have been expected.

Porous carbon is one of the novel carbon products obtained from the method using defluorination of PTFE by alkali metals[3-7]. First in this process, a mixture of carbon and inorganic alkali fluoride particle included in the carbon matrix is formed by defluorination of PTFE, and next, fluoride is removed by acid treatment to produce pore in the carbon. The resultant porous carbons are known to contain both micro- and mesopores with specific surface area of more than $2000m^2/g$. It is interesting that such the large surface area of carbon can be achieved at relatively low temperature, from room temperature to 473K, without any activation process at higher temperature.

The authors have examined various experimental conditions for defluorination of PTFE to control the pore of resultant porous carbon[8-10]. In the present work, we report that synthesis of carbon having mesopores with equal size was tried by the method using defluorination of PTFE by alkali metal together with a technique of physical vapor deposition(PVD) of PTFE. Recently, regular ordering of pore in porous carbon has been achieved by using various inorganic template materials during carbon formation[11]. The method using defluorination of PTFE also include a similar process that inorganic "template" fluoride particles are removed from the carbon matrix to form pores. Hence PVD of PTFE was tried to get a raw material for defluorination with well ordered molecular stacking of PTFE since it might be suitable for formation of a uniform fluoride template particles during the defluorination.

Experimental

Low PTFE used for PVD is a commercially available PTFE oligomer (CEFRAL LUBE V, Central Glass Co. Ltd.) with the average molecular weight of ca.10000, and PVD apparatus used in the present work is hand-made by Ulvac Inc. The schematic illustration of the PVD apparatus is shown in Fig. 1. A crucible with 2cm of inner diameter and 3cm of depth was filled with the low PTFE powder and twisted by heating wire, and placed at the bottom of the chamber. Quartz glass substrate plates were hung right above the lower crucible. After decompressing of the chamber, PTFE was heated gradually up to 573K by over 2 hours and the shutter was opened only from 473K to 573K to deposit the PTFE on the glass substrate. Total volume of PTFE deposited was adjusted according to the distance between low PTFE and substrate, and the thickness of PTFE deposited was roughly estimated by the simple deposition monitor. The morphology of the PTFE deposited on substrate was characterized by scanning electron microscope(SEM) .

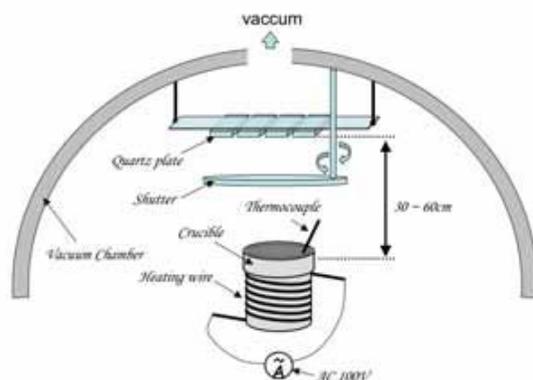


Figure 1. Schematic illustration of PVD apparatus used in the present work.

Next, the deposited PTFE was defluorinated with the state where it was still attached to substrate by potassium vapor at less than 473K (less than the temperature of PVD) in the inside of glass tube sealed under vacuum. After the defluorination, the product was dipped in 1M HCl one night to remove potassium fluoride by-product, washed in water and dried in air. The morphology of resultant carbon was characterized by transmission electron microscope (TEM). Commercially available PTFE powder (MJ1500, Mitsui-Dupont Fluorochemical Co.Ltd.) was also used for defluorination and compared with that deposited by PVD.

Results and Discussion

In Fig. 2, SEM pictures of PTFE deposited on the quartz glass are shown. Three glass substrates were hung in the chamber at different positions with equal intervals from the raw PTFE to obtain three samples with different volumes of PTFE deposition. In the SEM picture of the sample with the fewest PTFE, small PTFE flakes were clearly found to be deposited with standing sparsely and perpendicularly to the glass substrate. As the quantity of deposited PTFE increased, numbers of the flake increased and the

flakes were deposited in heaps on the substrate finally, but no strong connection between the each PTFE flakes to form a film was achieved after all since the PTFE powder deposited on the glass was separated easily. It is concluded from the SEM result, highly dense film of PTFE could not be synthesized with this technique and only vapor deposition of PTFE powder was possible. However, there must be some effects on reconstruction of the PTFE to have a high orientation of the molecules in the each particle by vapor deposition.

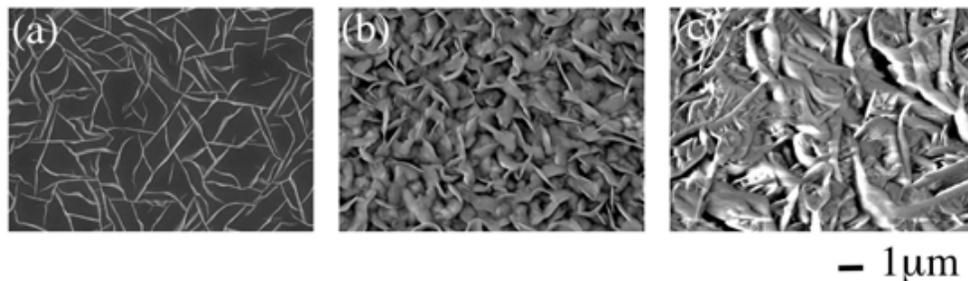


Figure 2. SEM images of PTFE deposited on quartz glass plate. The rough thickness of PTFE deposited are (a)0.1µm, (b)0.8µm and (c)9µm..

TEM pictures of the resultant carbon products from deposited PTFE and commercially available one are shown in Fig. 3, respectively. Porous carbon containing micro- and mesopores are known to be produced from deflorination of PTFE by alkali metals, and both pictures show the image of carbon including mesopores. However, there was a quite clear difference on the degree of porous uniformity between the deposited and commercially available PTFEs. The porous carbon from deposited PTFE had relatively uniform mesopores with the pore diameter of ca.10nm as shown in Fig. 3(a), compared with that from commercially available PTFE which showed images of meso- and even macropores with various pore diameters in the TEM picture of Fig. 3(b). In addition, the thickness of carbon wall from deposited PTFE was also uniform all over the carbon particle compared with commercial one having unevenness in the thickness.

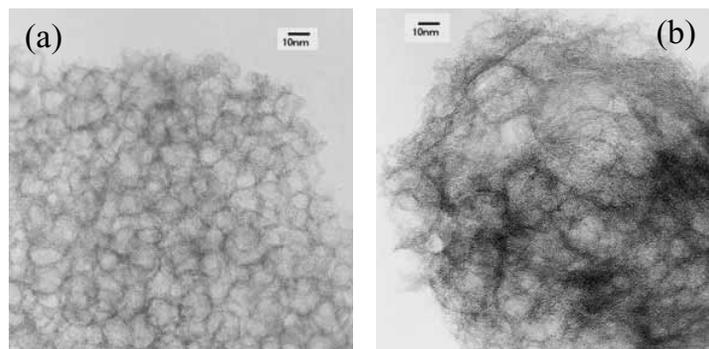


Figure 3. TEM images of porous carbons from (a) deposited PTFE and (b)commercially available PTFE powder.

Generally, mesopore and macropore produced by this method, defluorination of fluoropolymer, are considered to correspond to “marks” where KF particles are removed from carbon matrix by acid treatment. Therefore, improvement in the degree of uniformity on the size of the mesopore is considered to be achieved by making the generation and the growth of KF particles uniform during defluorination of PTFE. PVD in the present work did not make a beautiful film of PTFE, but at least gave an effect as distillation and recrystallization of PTFE on the substrate, which seems to make the molecular orientation and density more uniform in each one flake of deposited PTFE. Hence, the KF particles grew in the carbon matrix uniformly during the defluorination.

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