Carbon Fibers: II. Oxidation of Pitch and PAN Fibers

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Introduction

In the first presentation, the physical characterization of pitch and PAN fibers was discussed, and it was concluded that both fibers had essentially the same BET surface area; 0.5 m2/g and a comparable total pore volume less than 0.003 cc/g. This presentation summarizes the results obtained from experiments aimed to determine the Active Surface Area, ASA, of the fibers. The ASA is an arbitrary parameter which includes the sum of areas of active sites at the edges of basal planes of the fiber crystallites, including vacancies and imperfections. The ASA has been found to be an excellent index of reactivity of several carbonaceous materials at elevated temperatures. [1] Traditionally, the ASA is determined by subjecting the carbonaceous material, held at 300C, to molecular oxygen for 24 hr at a starting pressure of 0.067 KPa. The carbon is then heated to 950 C and the desorbed amounts of CO and CO2 are collected and quantified. The amount of oxygen that had been chemisorbed by the sample, and desorbed as CO and CO2, is calculated. By assuming that each oxygen atom is attached to one carbon site, and that the average area occupied by one active carbon site is 0.083 nm2, the value of ASA is computed. [1]

Experimental

A volumetric glass adsorption apparatus (Figure 1) was used. The sample was placed horizontally in a quartz boat, evacuated to 10 $^{-9}$ KPa, heated in vacuum at 20°C/min to 1000°C, held at this limit for 1 h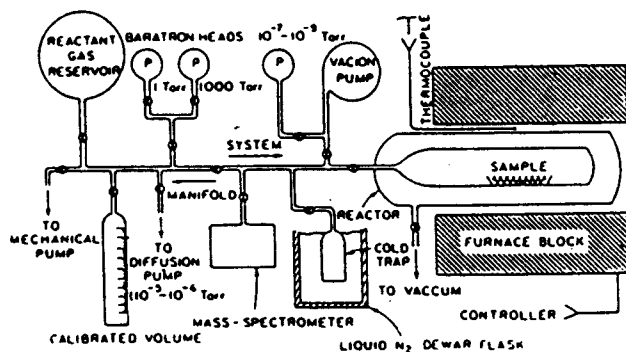r, and finally cooled to 300°C. Oxygen was then admitted to the sample at a starting pressure of 0.067 - 13.3 KPa. For most of the runs, the exposure time was either 16, 40, or 64 hrs, however, for a few runs, the exposure time was longer. At the end of this interval, oxygen was pumped away and the procedures developed by other investigators were essentially followed. [1,2]

Results and Discussion

During oxygen chemisorption measurements, significant amounts of CO2 were liberating during the tests; thus indicating that the samples were gasifying during ASA determination. Apparently, the amount gasified was dependent on the starting available ASA, and that the computed value of ASA was dependent on the amount of CO2 liberated from previous runs. That is, while attempting to determine the ASA of the fiber, the ASA was constantly increasing as the tests progressed. Figure 2 shows the data obtained for the as received T-300 fiber at a starting pressure of 0.67 KPa. For those tests having an exposure time of 16 hr, a linearity was observed between the apparent value of ASA and the number of CO2 moles gasified. Extrapolation to zero level of gasification would give the actual value of ASA; 0.039 m2/g, which would have been obtained if gasification were not taking place. Another linearity was observed for exposure times of 40 and 64 hr, however, with a higher intercept value of 0.075 m2/g. This implies that an exposure time of 16 hr was not long enough to cover the entire available ASA. As the tests progressed, the generated amounts of CO2 kept increasing, and the apparent values of ASA

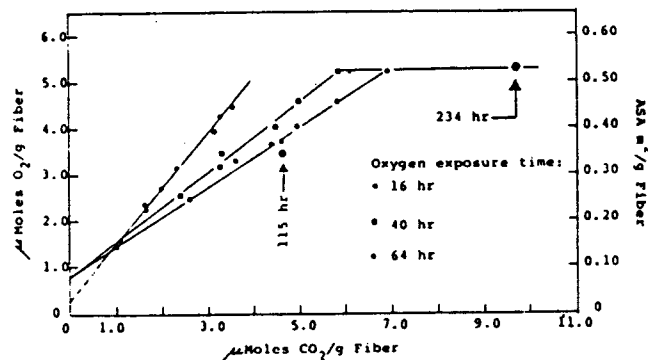Figure 1. Apparatus used to determine Active Surface Area (ASA) of carbon fibers.

Figure 2. ASA data for the as-received T-300 fiber.

increased monotonically before attaining a constant value of 0.53 m2/g. At that point, the ASA remained unchanged. Thus, as Figure 2 shows, the final apparent value of ASA at 40, 64, or 234 hr exposure time became independent of exposure time or of the amount of CO_2 gasified. It comes as no surprise that this final value of ASA approaches the BET area (0.56 m2/g) because in x-ray diffraction studies this fiber gave no diffraction pattern, thus indicating it was a non-crystalline material.[3] For the as-received VSB-32 fiber, the extent of gasification, at a starting oxygen pressure of 0.67 KPa, was insignificant, and the average ASA values were 0.024 m2/g at 16 hr and 0.028 m2/g at 40 and 64 hr exposure times. This value remained constant even after the samples had been subjected to successive chemisorption/desorption cycles with a final total oxygen exposure time of about 700 hr. It is noted that the true value of ASA of the as-received T-300 fiber is 268% higher than that of the VSB-32. Since the ASA is an acceptable index for predicting the reactivity of carbonaceous materials at elevated temperatures, it means that the PAN fiber would be more susceptible to rocket nozzle firing conditions than the pitch fiber.

Now we consider the case of the graphitized VSB-32 sample and the effect of pressure on ASA. Figure 3 displays the relations between the apparent values of ASA and the amounts of CO_2 generated at different pressures. At 0.067 and 0.67 KPa the apparent value of ASA is independent of the amount of CO_2. At higher pressures, however, there exist linearities between ASA and the number of CO_2 moles generated, the higher the starting oxygen pressure, the higher was the slope of the line. Evidently all the lines intercept at a constant value of 0.019 m2/g which is assigned here as the true value of ASA for the graphitized VSB-32 fiber. It is clear that for a starting oxygen pressure of 0.67 KPa or below, the concurrent gasification reaction, taking place with oxygen chemisorption, does not increase the starting number of active sites at the fiber surface. Most likely, those fresh active sites generated behind the CO_2 molecules were instantaneously annealing out, thus preserving the original structure of the fiber. On the other hand, at higher pressures (2.67 and 13.33 KPa), the rate of generating active sites exceeded the rate of their disappearance and, hence, a greater number of active sites was detected as the tests progressed. The results for the graphitized T-300 fiber are shown in Figure 4. For a starting oxygen pressure of 0.067, 0.67, and 2.67 KPa, there exists one linearity between the apparent values of ASA and the corresponding numbers of CO_2 moles generated. That is, the linearity was independent of pressure. Extrapolation to the zero level of burn-off gives the

true value of ASA in absence of gasification. This value is 0.024 m2/g. At higher pressure (13.33 KPa), however, the apparent value of ASA is drastically higher (0.127 m2/g) yet, it became independent of the amount of CO_2 generated. It is possible that oxygen chemisorption at this pressure or above, would cover, in addition to the sites that had been covered at lower pressure, additional groups of "less" active sites which were not reached at lower pressures. Verification of this hypothesis is currently underway. It is known that graphitization of carbon fibers increases both the degree of crystalinity and the size of crystallites, and as a consequence, it decreases the area of active sites at the edges of basal planes. This is clearly evident from the present results. Upon graphitization, the true values of ASA decreases from 0.075 to 0.024 m2/g for the T-300 fiber, and from 0.028 to 0.019 m2/g for the VSB-32 fiber. In either case, the PAN fiber has more ASA than the pitch fiber, and, therefore, the PAN fiber would be more susceptible to rocket nozzle firing conditions than the pitch fiber.

Conclusions

The present study suggests that the procedure required to determine the true ASA of carbon fibers is different than that used for other carbonaceous materials; it dictates the need to account for the amount of CO_2 gas generated during the exposure of the fibers to oxygen at 300°C. This early gasification reaction is, in many cases, responsible for generating additional active sites which, in turn, may give a higher apparent value of ASA. The dependence of ASA on the number of CO_2 moles generated during oxygen exposure is generally linear with an intercept (at zero level of gasification) that gives the actual value of ASA. Although the apparent value of ASA appears to increase with the starting oxygen pressure, the true ASA value is independent of pressure up to 2.67 KPa.

References

1. N. R. Laine, F. J. Vastola, and P. L. Walker, Jr, J. Phys. Chem. 67, 2030, 1963.

2. W. P. Hoffman, and J. A. Lowry, Extended abstract, 16th Biennial Conference on Carbon, 1983, p. 357.

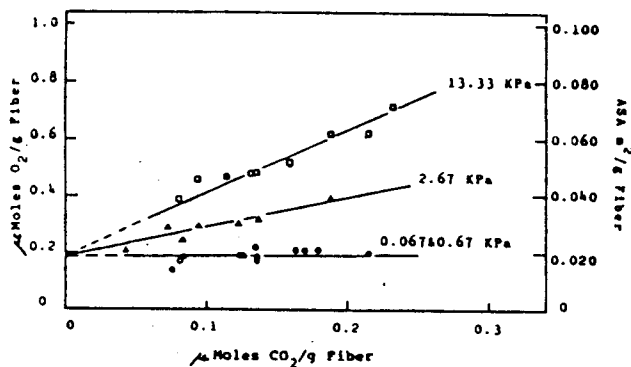3. P. A. Thrower, The Pennsylvania State University, Private Communication.
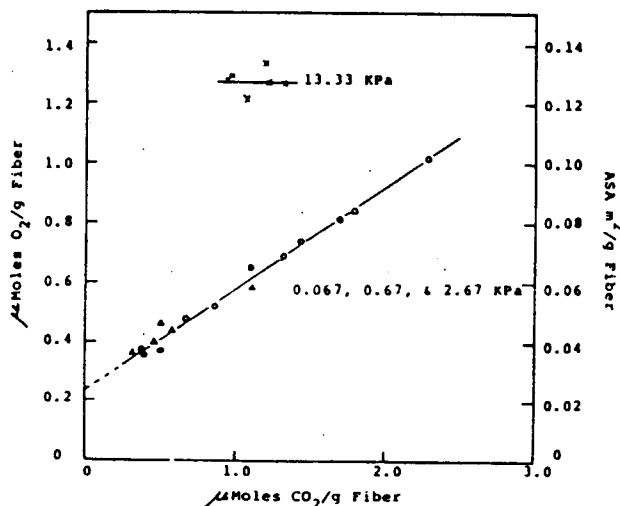
Figure 3. ASA data for graphitized VSB-32 fiber.

Figure 4. ASA data for graphitized T-300 fiber.