INFLUENCE OF SURFACE CHEMISTRY ON THE PREPARATION OF A STABLE, BLISTER-FREE FLEXIBLE GRAPHITE

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Introduction

Flexible graphite has been manufactured by UCAR Carbon Company Inc. for fluid sealing and automotive gasket applications since 1968 [1]. A characteristic of all flexible graphite when rapidly heated to a high temperature (900°C), is its tendency to blister, a delamination of the mechanically weak basal planes. Blistering occurs in flexible graphite when diffusion of thermally activated gas (mostly physically and chemically adsorbed water) is too slow to release the internal pressure. Physical approaches can be used to relieve the internal pressure such as decreasing its standard density, decreasing its thickness, and by puncturing its surface [2]. This paper describes a chemical approach to produce a stable, blister-free flexible graphite by modifying its surface chemistry.

Experimental

Although flexible graphite possesses only a very low surface area (10-20m^2/g), and relatively small amounts of surface functionality, a gravimetric test was devised that relates to the degree of acidity or basicity of a flexible graphite's surface functional groups (Figure 1). The weight change after 900°C heat treatment and equilibration (approximately 30 minutes) in the environment (Figure 1) is due to a change in the amount of adsorbed moisture, which in turn is related to the degree of acidic or basic characteristics of the evaluated flexible graphite's surface functional groups. When using this test, a smaller weight change (< 0.1%) after the 900°C heat treatment and equilibration indicates a basic, hydrophobic flexible graphite surface, while larger weight change suggests an acidic, hydrophilic surface. The flexible graphite specimens evaluated were 0.015" thick and 1.1 g/cc dense.

The flexible graphites were either hydrogenated (5 SCFH) in a nitrogen-purged induction furnace at 1000°C or chlorinated at 1700°C in order to produce a stable, blister-free flexible graphite.

Results and Discussion

Morimoto et al. showed that the adsorption sites for water adsorption on the surface of graphite can be reduced by heat treatment [3]. Therefore, a low-density flexible graphite (0.05 g/cc) was heat treated from between 500°C to 900°C at 100°C increments for 30 minutes. After heat treatment, the lower-density flexible graphites were compressed to a standard higher-density flexible graphite (1.1 g/cc). These flexible graphites did not blister when the heat treatment increased to 900°C. However, the blister-free status of the flexible graphite was only temporary for approximately 3 or 4 months.

The mechanism for blistering reduction can be proposed from Papier's et al. work [4]. They showed that acidic surface functional groups, such as carboxylic acids, lactones, and phenols, present on all carbons, decompose to form a basic surface group, pyrone. The acidic surface functional groups are hydrophilic, which most likely promote blistering while the basic groups are hydrophobic. Bansal et al. [5] further showed that the base adsorption capacity of an activated carbon diminished as the temperature of activation increased to 800°C, a temperature consistent with the reduction of blistering tendency of the flexible graphite at 900°C.

The blister-free flexible graphite, only temporary, suggests that the 900°C flexible graphite is unstable, and that the surface chemistry is changing, presumably by reaction with oxygen, water, or CO_2 in the air. A surface stability study using the above simple gravimetric test confirms (Figure 2) that the surface is changing and becoming more acidic with time. Additional surface modifications are required to stabilize its surface.

Puri and Bansal [6] reported that the active sites on heat-activated carbon surfaces behave as olefinic sites. Tobias and Soffer [7] further classified the active sites as nonconjugated olefinic bonds, surface-free electrons, or distorted graphite pi bonds. Therefore, a heat-treated flexible graphite was subjected to an additional reaction with either H_2 or Cl_2 gas. The resulting flexible graphites were found blister free and stable for at least a year, the duration of our testing. The surface stability study of the hydrogenated flexible graphite (Figure 3) confirms that the surface chemistry is basic and stable. Recently, Menéndez et al. [8] have created a stable, basic activated carbon by similar reactions.

Conclusions

Although the surface area of flexible graphite is extremely low, and the amount of surface functional groups are small, the constitution of these functional groups are extremely sensitive to the flexible graphite's blistering. A stable, blister-free flexible graphite is prepared by subjecting it to two reactions: a high-temperature heat treatment which produces a basic surface, followed by a stabilizing reaction such as addition of hydrogen to the active sites generated during the high-temperature heat treatment [9].

References

1. Shane, J. H., Russell, R. J., and Bochman, R. A., U. S. Patent 3,404,061 (1968).
2. Lohrke, J. L., Sterry, J. M., and Lyons, M. D., U. S. Patent 4,752,518 (1988).
3. Morimoto, T. and Miura, K., *Langmuir*, 1987, 1, 658.
4. Papier, E., Li, S. and Donnet, J. B., *Carbon*, 1987, 25, 243.
5. Bansal, R. C., Bhatia, N., and Dhami, T. L., *Carbon*, 1978, 16, 65.
6. Puri, B. R. and Bansal, R. C., *Carbon*, 1966, 3, 533.
7. Tobias, H. and Soffer, A., *Carbon*, 1985, 23, 291.
8. Menédez, J. A., Phillips, J., Xia, B. and Radovic, L. R., *Langmuir*, 1996, 12, 4404.
9. Greinke, R. A. and Bretz, R. I., U. S. Patent 5,582,811 (1996).

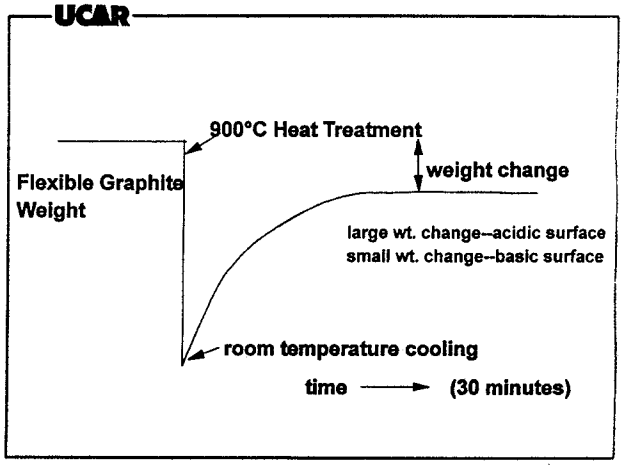

Figure 1. Flexible graphite surface test.

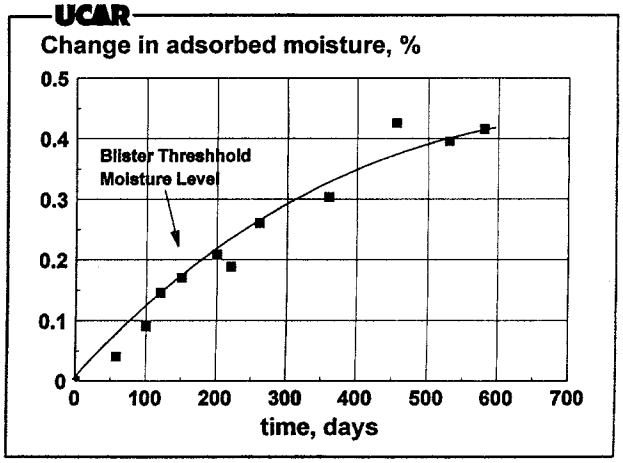

Figure 2. Surface stability study with 900°C heat-treated flexible graphite.

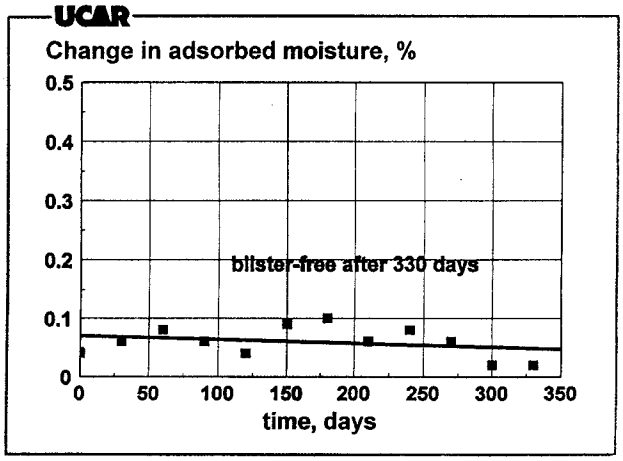

Figure 3. Surface stability study with 1000°C hydrogenated flexible graphite.