

CHEMICAL CHARACTERIZATION OF C/C COMPOSITES AFTER BRAKING SOLICITATION

JC. Rietsch, J. Dentzer, R. Gadiou, Cathie Vix-Guterl, Institut de Chimie des Surfaces et Interfaces, 15 rue Jean Starcky – BP 2488 - 68057 Mulhouse, FRANCE

P. Jacquemard, Messier-Bugatti – Division Carbone Industrie, 7 avenue Bel Air – 69627 Villeurbanne, FRANCE

Introduction

C/C composites are well adapted to aircraft braking applications. Their low density, high thermal conductivity and heat capacity, high temperature resistance, make them attractive for safe high energy braking. However, they are sensitive to environmental conditions such as the oxygen or water content in ambient air. [YEN95, CHEN94, ROBERT94] This work concerns the study of the surface chemistry and structural organisation of the rubbing surface of a C/C disk. The experiments were realized directly on the whole reduced scale braking disk thanks to TPD-MS and ASA measurements, respectively. Recently, authors presented studies on the surface chemistry of wear debris [JOLY06] and the chemistry of the interface debris (also called 3rd body) thanks to a brushing of the surface [PESZY06]. However, the brushing of the rubbing surface is tricky and sometimes even impossible due to the small amounts of 3rd body. In this study, the surface chemistry and structural organisation of the rubbing interface is studied directly on the whole disk thanks to adapted experimental devices.

Experimental

Material

The experiments were carried out on a 3D-Carbon/Carbon composite made from poly-acrylonitril-based fibres embedded in a chemical infiltrated carbon matrix. The surface properties of two materials are discussed here: an unworn and a worn C/C composite.

Braking tests

Braking tests were carried out on a reduced scale dynamometer. Experiments were conducted at a constant normal pressure $P = 6\text{bar}$. Each braking experiment is composed of a large number of identical stops in order to achieve a reproducible state concerning wear and friction coefficient. Each stop is followed by a cooling period allowing the disks to achieve the starting temperature of 50°C . The temperature is measured by a thermocouple placed at 1,5mm from the sliding surface. The test results presented in this work correspond to a low braking energy, equivalent to a cold taxiing in the aeronautical field.

Study of the surface chemistry by TPD

Temperature-programmed desorption (TPD) was performed in a vacuum system equipped with a mass spectrometer at a maximum pressure of 10^{-4} Torr. The whole C/C composite was deposited in a large fused silica tube and heat-treated up to 950°C with a linear heating rate of $0.6^\circ\text{C}\cdot\text{min}^{-1}$. During the experiment, the gas phase was continuously analyzed quantitatively by the mass spectrometer. Before the experiment, the mass spectrometer was calibrated using H_2 ($m/z = 2$), H_2O ($m/z = 18$), CO ($m/z = 28$), N_2 ($m/z = 28$), O_2 ($m/z = 32$), and CO_2 ($m/z = 44$) gases. The quantitative determination of functional groups was based on H_2 , H_2O , CO , and CO_2 , as the amount of O_2 and N_2 was found to be negligible. The total gas pressure evolved during the heat treatment was measured as a function of the temperature using a Bayard-Alpert gauge. The total gas pressure was compared to the pressure calculated from the sum of the partial pressure of the gas species deduced from the quantitative analysis of the gas phase.

Study of the structural organisation through the determination of the active surface area (ASA)

The active surface area was measured by oxygen chemisorption in the same experimental set-up as for the TPD analysis. In this case, the sample is heat-treated under vacuum up to 950°C to clean the surface. After cooling down at 300°C , oxygen is introduced in the reactor at a pressure of 66.5 Pa causing a chemisorption of O_2 on the C/C composite surface. The O_2 chemisorption lasts 10 h at 300°C and leads to the formation of surface oxide complexes at a specific part of the whole composite surface area, i.e. the composite active sites area. By thermal treatment between 300 and 950°C of the sample, the oxygen complexes are decomposed into CO and CO_2 which amounts are determined by mass spectrometry. By determining the number of moles of each gas desorbed and taking the area of an edge carbon site that chemisorbed an oxygen atom as 0.0083 nm^2 , the surface area occupied by chemisorbed oxygen can be calculated [LAINE63].

Results and discussion

Comparison of the surface chemistry of an Unworn / Worn C/C composite

The surface chemistry of an unworn and a worn disk is compared in order to investigate the surface chemistry modifications induced by the friction.

The desorption rates of the H₂O, CO, CO₂ and H₂ gases as a function of thermal treatment are presented in **Figure 1.** and **Figure 2.** for both materials.

The unworn material (**Figure 1.**) desorbs essentially large amounts of water especially before 300°C, mainly attributed to physisorbed water trapped into the material porosity and/or fixed in the experimental set up. On the contrary, the desorption of CO and CO₂ is negligible, meaning that the amount of oxygen functional group at the carbon surface is low. The H₂ desorption is also negligible until 850°C, it slightly increases above this temperature probably mainly due to structural rearrangement.

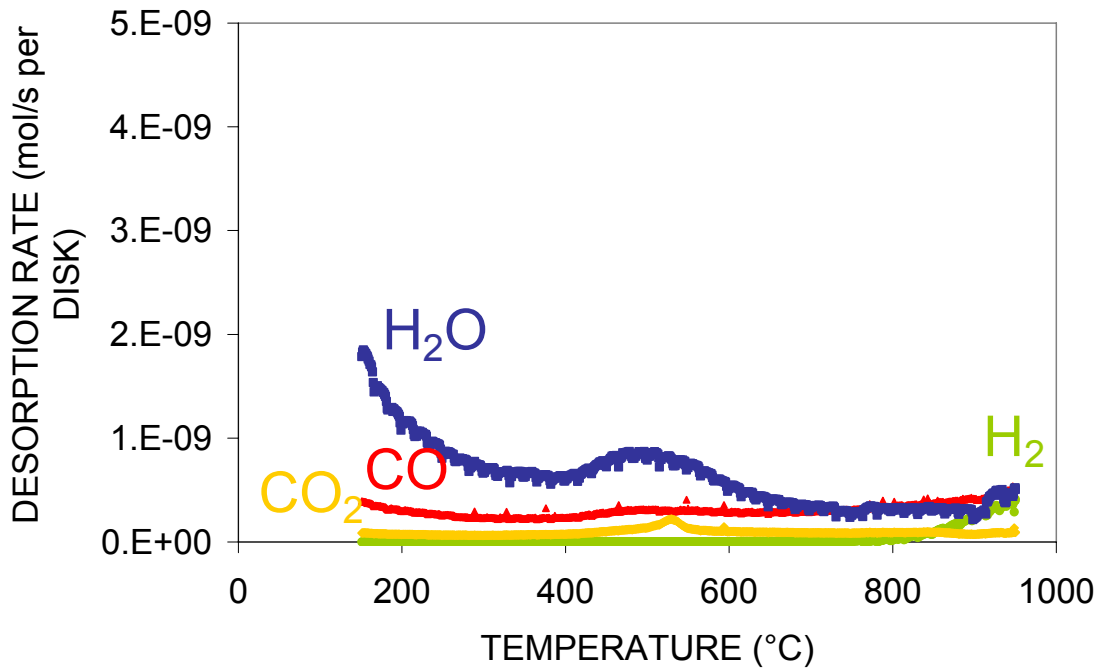


Figure 1. TPD curves of the unworn material

The TPD curves obtained for the material rubbed in a low braking energy condition are shown in **Figure 2.** CO and CO₂ are released in a wide range of temperature, indicating the presence of oxygenated functions on the rubbed surface. These profiles are very similar to those already observed on wear debris [JOLY06] or on activated carbons. The fact that the CO and CO₂ peaks are broad reveals a diverse surface chemistry composed of low thermal stability functions such as carboxylic acids but also of high thermal stability functions such as quinones or ethers [FIGUEI99].

The H₂ curve profile is also very different from the profile of the unworn material. Actually, the H₂ desorption already starts at 600°C (vs. 850°C for the unworn material) and the desorption rate is much higher. In this case, we assumed that the H₂ release mainly results from the reaction between water and carbon due to carbon grinding in wet atmosphere.

The H₂O curve profile is similar to the unworn one confirming large amounts of trapped water in the composite porosity or in the TPD-MS oven.

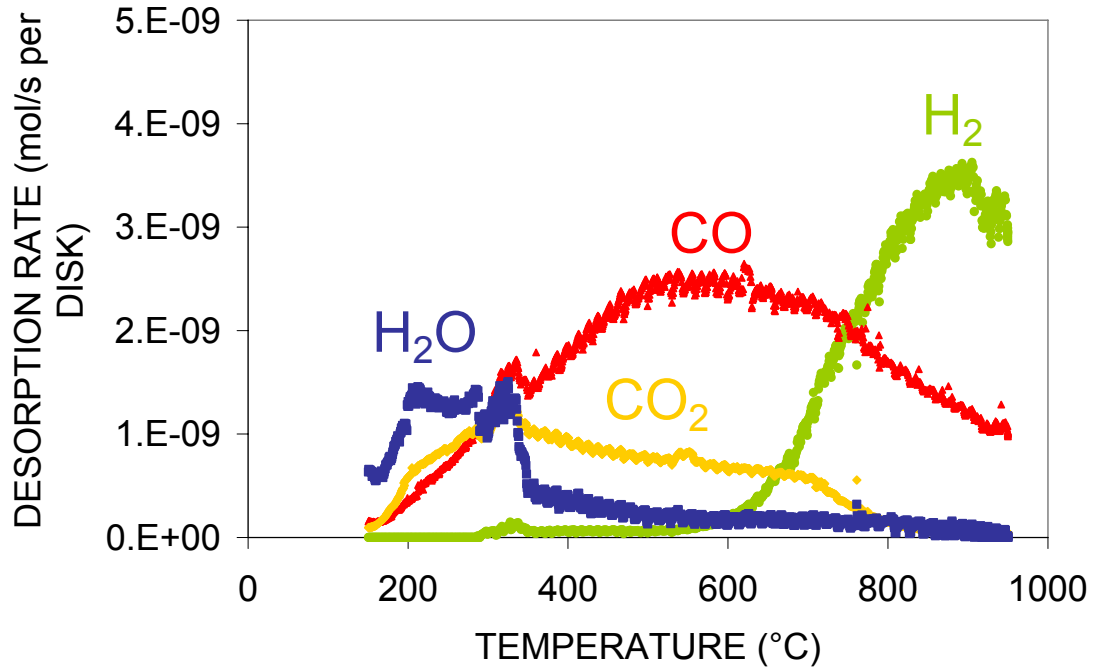


Figure 2. TPD curves of the worn material (cold taxi condition)

	Unworn	Cold taxi
CO ₂ μmol/disk	4	44
CO μmol/disk	13	130
H ₂ O μmol/disk	45	54
H ₂ μmol/disk	1	37

Table 1. Total amounts of CO, CO₂, H₂O and H₂ desorbed for the unworn and worn material

The total amount of each gas desorbed are compared in **Table.1** (calculated from the time integration of the desorption rate curves). As suggested by the TPD curves, the amount of gases released increases significantly after rubbing the disk. After rubbing, the amount of CO and CO₂ is about 10 times higher and 37 times higher for H₂, whereas the H₂O quantity is almost similar.

Additional experiments have shown that the surface chemistry evolution that we observed is mainly due to the third body; the evolution of the first body in the same rubbing conditions being negligible. The 3rd body on C/C composites and graphites was defined in the literature as the carbon dust formed during the rubbing and trapped at the contact interface.

ASA comparison between the unworn/and worn composite

An important increase of the active surface area is observed (**Table.2**) after rubbing the disk. The 4 times higher ASA indicates that the 3rd body is mainly constituted of carbon with a low structural organisation which is therefore much more reactive than the thirst body.

	Unworn	Cold taxi
ASA m ² /disk	0,2	0,8

Table 2. ASA for the unworn and worn material

Conclusion

The surface chemistry investigations by TPD-MS showed important qualitative and quantitative discrepancies between worn and unworn materials. The apparition on the carbon surface of functional oxygenated groups after rubbing has been demonstrated. These new functional groups are formed by reaction between carbon and the gaseous environment (O_2 and H_2O). The location of these new chemical functions was found to be at the rubbing interface and was mainly attributed to the presence of the third body. The ASA measurements indicate that the third body is mainly constituted of low organised carbon. Finally, this study points out that the TPD analysis on the whole C/C disks is sensitive enough to follow the modifications of the surface properties of the carbon after rubbing.

References

- Chen, J.D. 1994 Friction and wear of PAN/pitch-, PAN/CVI- and pitch/resin/CVI- based carbon/carbon composites, *Wear*, 174 :129-135
- Figueiredo, J. L. Modification of the surface chemistry of activated carbons. *Carbon*. 37: 1379-1389
- Joly, JP. 2006. A temperature-programmed desorption and oxidation investigation of wear debris from carbon/carbon composite aircraft brakes. *Carbon*, 45: 124-131
- Laine, N.R.1963. *J. Phys. Chem.* 67: 2030–2034.
- Peszynska, K. 2006. Thermal analysis of bulk carbon-carbon composite and friction products derived from it during simulated aircraft braking. *Carbon*. Doi:10.1016/j.carbon.2006.10.025
- Robert, F. 1994. Combined influence of an inert gas environment and a mechanical action on a graphite surface. *Wear*. 181-183: 687-690
- Yen, B.K. 1995. Influence of water vapour and oxygen on the tribology of carbon materials with sp² valence configuration. *Wear*. 192: 208-215