

CARBON-CARBON BRAKE DEBRIS: OXYGEN GROUPS AND MEMORY FROM THE STARTING MATERIAL

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Introduction

The mechanism of C-C brake debris formation involves coupled mechanical and chemical effects. Therefore, the physicochemical characterization of debris is essential to understand friction and wear phenomena occurring during aeronautical brake operations. Although the role of physisorbed water and of the so-called chemisorbed oxygen in these phenomena has been recognized for a long time (Blanco *et al.* 1997; Chen *et al.* 1996; Yen and Ishihara 1996a; Yen and Ishihara 1996b; Yen *et al.* 1997), it is only recently that scientists undertook in-depth investigations about the chemical reactions occurring during braking tests. Thus, it has been shown that oxygen is consumed with a concomitant evolution of carbon dioxide during braking tests under high friction coefficient conditions (Gouider *et al.* 2004). Other authors (Vix-Guterl *et al.* 2005) have proposed to determine C-C material properties combining the "active surface area" concept, a concept generally used in the field of carbon combustion, and a "functional group approach" based on surface chemistry. More recently, it has been found that debris samples obtained during braking tests carried out under various simulated taxiing conditions are rich in oxygen, forming part of a wide variety of functional groups (Francois *et al.* 2007). This finding was extended shortly after (Peszynska-Bialczyk *et al.* 2007) for debris obtained during braking tests under simulated landing conditions. This work presents the results of a physicochemical study of ejected debris obtained with two C-C materials differing by their degree of graphitization. Braking tests were carried out under low energy, high friction coefficient conditions. These conditions, at low temperature, were chosen because they are convenient to study the coupling between mechanical and chemical effects occurring in braking processes.

Experimental

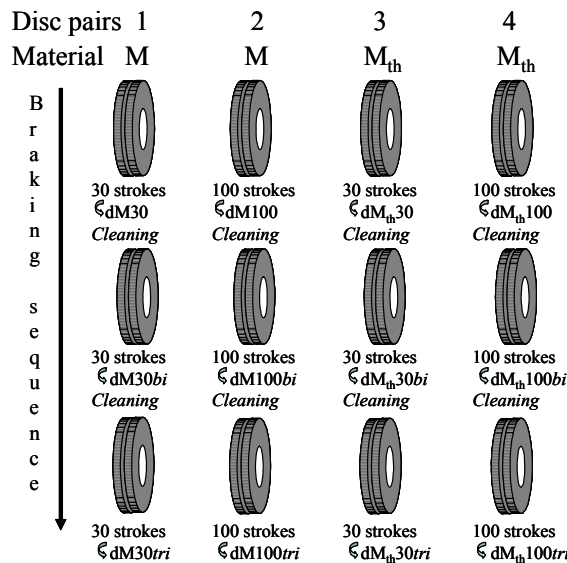


Figure 1. Sequences of braking tests for the production of debris sample from the four discs pairs.

A subscale dynamometer with a disc-on-disc configuration was used. This dynamometer has been described previously (Francois *et al.* 2007). Braking tests were performed with pairs of identical discs, which were 49 mm inner radius, 66.5 mm outer radius and 14 mm thick. Sequences of braking strokes were conducted from an initial sliding rate of 4.8 m.s^{-1} to complete stop with high friction coefficient ($\mu \approx 0,36$) and low temperature ($50\text{-}90^\circ\text{C}$) conditions. Relative humidity in air surrounding the discs was 20 %.

Two types of carbon-carbon materials, prepared by chemical vapour infiltration of pyrolyzed PAN preforms, were used. They will be referred as M and M_{th} hereafter. During disc manufacturing, material M_{th} was subjected to

higher temperatures than material M. Four pairs of C-C brake discs (see Figure 1) were used: two pairs made of material M and two other pairs made of material M_{th} . Each pair underwent either 30 or 100 consecutive braking strokes. Accordingly, samples of ejected debris were denoted dM_{30} , dM_{100} , $dM_{th,30}$ and $dM_{th,100}$. Then, the paired discs were cleaned in an ethanol ultrasonic bath for several hours and dried in a stove at 140°C overnight. Subsequently, the paired discs were submitted to a second series of braking strokes identical to that they previously underwent; the resulting debris samples were denoted dM_{30bi} , dM_{100bi} , $dM_{th,30bi}$ and $dM_{th,100bi}$. Finally, ultrasonic cleaning and drying was repeated once again before new identical braking tests, which produced debris samples denoted dM_{30tri} , dM_{100tri} , $dM_{th,30tri}$ and $dM_{th,100tri}$, were carried out. In summary, braking tests provided 12 different wear debris samples. In addition, saw dust samples, termed sM and sM_{th} , were obtained through a slow sawing of material pieces. Before any characterization experiment, debris samples were treated at 140°C overnight under air, in order to remove most of their moisture, and kept in stopped flasks.

Thermal decomposition of oxygen groups present in debris samples was investigated by means of a thermobalance coupled to a mass spectrometer (TG-DTP-MS). In a typical experiment, 10 mg of sample were placed in the thermobalance crucible. Experiments were performed at a heating rate of $20^{\circ}\text{C min}^{-1}$ up to 1200°C under 1.4 L h^{-1} flow rate of Argon. The mass spectrometer was calibrated with calcium oxalate.

Results and discussion

Structure

Figures 2 and 3 show the X-ray diffraction patterns for the raw materials, sM and sM_{th} , and for the corresponding ejected wear debris collected after 30 braking strokes from the discs re-used once. As expected, sample sM_{th} , which has been treated at higher temperature, presents a much sharper (002) reflection than sample sM . This means that it is much more ordered. The diffraction patterns of debris are quite different: The peaks close to $2\theta \approx 26^{\circ}$ are much weaker for debris samples than for the parent materials, the peak at $2\theta \approx 43^{\circ}$ is not seen any more. A very broad feature attributable to a disorganized solid is observed for $2\theta < 30^{\circ}$.

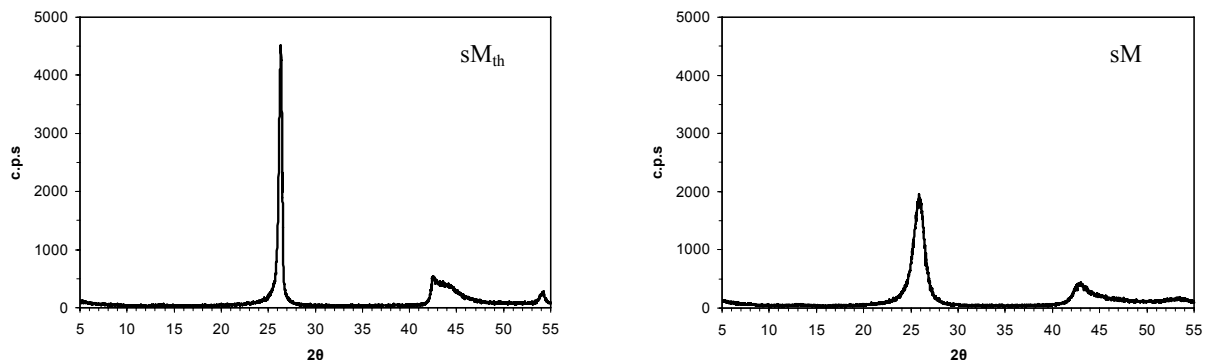


Figure 2. XRD patterns of raw materials

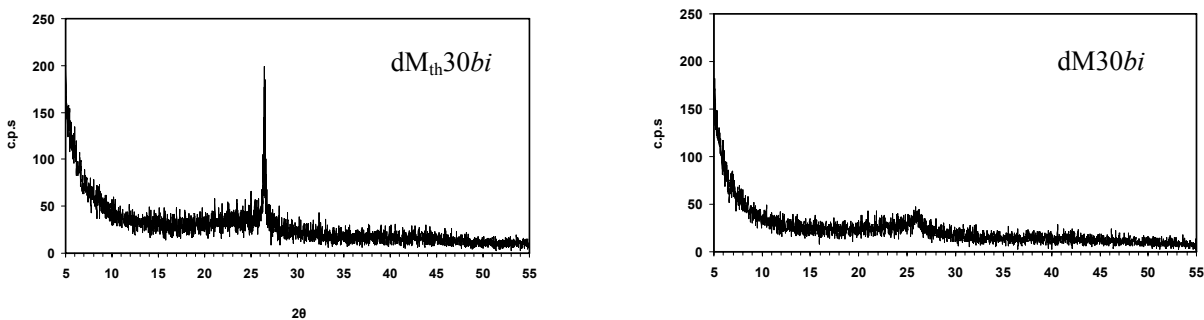


Figure 3. XRD Patterns of debris from material M and from material M_{th}

Specific surface area

Table 1 gives the BET specific surface areas of sawn raw materials and debris samples. Debris samples have much larger specific surface areas than sawn samples, supposed to be characteristic of original materials. This property has been mentioned previously (Francois et al. 2007) but the originality of the present results is that samples issued from the graphitized material M_{th} systematically exhibit larger specific surface areas than those issued from material M. A characteristic difference of $60 \text{ m}^2/\text{g}$ may be assessed from the mean values for samples dM and for samples dM_{th} .

Table 1. Specific surface area (m^2/g) of sawn and debris samples.

sM	sM _{th}	dM	dM	dM	dM	dM	dM	dM _{th}	dM _{th}	dM _{th}	dM _{th}	dM _{th}	dM _{th}
		30	30	30	100	100	100	30	30	30	100	100	100
			<i>bi</i>	<i>tri</i>		<i>bi</i>	<i>tri</i>		<i>bi</i>	<i>tri</i>		<i>bi</i>	<i>tri</i>
44	33	167	171	157	146	171	160	284	198	204	256	216	197

Chemistry

Figure 4 shows, as an example, the TPD profiles of H_2O , CO and CO_2 for the debris of both materials M and M_{th} after 30 braking strokes. Results are shown for debris obtained from the original discs and also from the same discs re-used once and twice after intermediate ultrasonic cleaning.

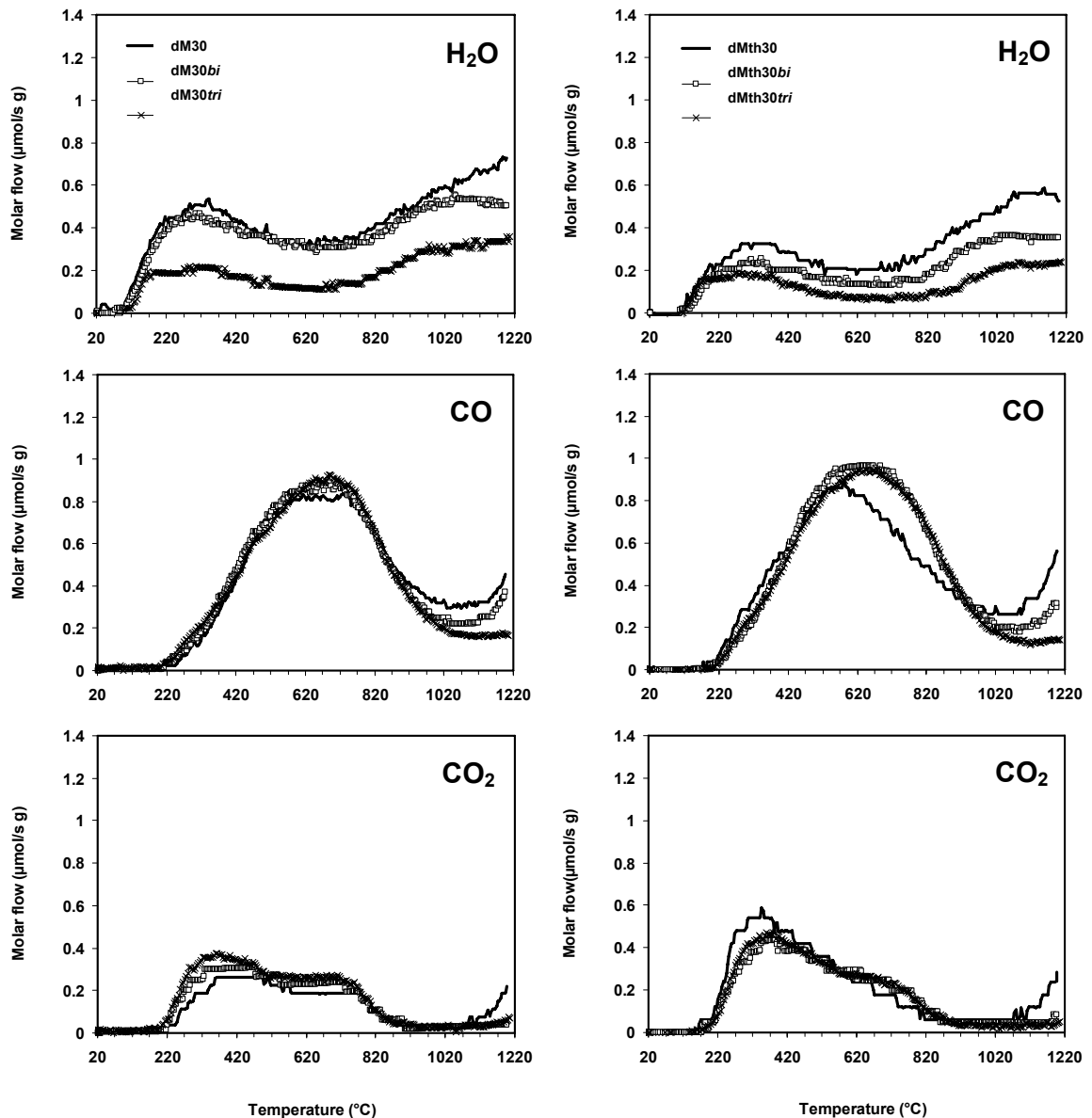


Figure 4. TPD profiles of water and carbon oxides for ejected debris samples collected at the end of the three series of 30 braking strokes

It is now generally acknowledged that TPD profiles like those presented in Figure 4 are due to the thermal decomposition of a variety of oxygen groups decorating the rims of graphene layers (de la Puente *et al.* 1997; Figueiredo *et al.* 1999; Haydar *et al.* 2000; Szymanski *et al.* 2002). An interesting feature in CO₂ profiles is that the first broad desorption peak at about 350°C is higher for debris samples M_{th} than for debris samples M. This means that debris M_{th} exhibit larger amounts of carboxylic groups than debris M. Finally, large amounts of H₂ (not shown in Figure 4) are evolved in a peak starting at 600°C with a maximum at about 850°C. Similar results for CO, CO₂, H₂O and H₂ were found for debris samples collected after series of 100 braking strokes.

Table 2. TPD results: Amount of CO, CO₂ and H₂O evolved from debris samples between 25 and 1200°C.

	sM	sM _{th}	dM	dM	dM	dM	dM	dM	dM _{th}	dM _{th}	dM _{th}	dM _{th}	dM _{th}	dM _{th}	
			30	30	30	30	100	100	100	30	30	30	100	100	100
			bi	tri	tri	100	bi	tri		bi	tri	100	bi	tri	
CO (mg/g)	9.4	6.2	81.6	79.5	77.1	61.1	80.3	70.3	82.4	86.3	81.2	91.8	90.7	81.2	
Mean value (mg/g)						75.0						85.6			
CO ₂ (mg/g)	7.4	2.0	42.3	41.1	46.7	32.5	48.2	41.2	61.3	52.0	51.9	81.1	54.2	43.7	
Mean value (mg/g)						42.0						57.4			
H ₂ O(mg/g)*	7.1	ε	29.1	30.5	7.4	15.9	15.0	3.1	19.0	9.8	ε	31.7	8.2	2.7	
Δm(SM)(mg/g)	2.4	0.8	15.3	15.1	13.1	10.9	14.4	11.5	16.3	14.8	13.3	20.5	15.3	12.8	
Δm(TG)(mg/g)	0.8	0.6	17.0	14.9	13.5	13.5	15.5	13.0	19.5	16.7	14.6	21.0	17.5	14.4	
Δm(TG)-Δm(SM)	-1.6	-0.2	1.7	-0.2	0.4	2.6	1.1	1.5	3.2	1.9	1.3	0.5	2.2	1.6	
Mean value (mg/g)									1.5						

* Amount corrected by subtraction of water released in a blank experiment without sample

The amounts of H₂O, CO and CO₂ desorbed from all the samples in the temperature range 25-1200°C are shown in Table 2. First of all, it should be highlighted that the mass losses, Δm(TG), provided by the thermobalance are in good agreement with those, Δm(SM), calculated from the TPD results; mass losses provided by TG are generally slightly lower than those calculated from the amounts of CO, CO₂ and H₂O determined by TPD-MS. This is due to the amount of desorbed hydrogen that has not been quantified in this work. This amount may be assessed at 1.5 mg/g from the mean value of the difference Δm(TG)-Δm(SM). The amounts of desorbed water largely fluctuate from one sample to another. This is due to the fact that debris samples capture variable amounts of water during their handling: Indeed oxygen-rich carbonaceous materials are hydrophilic (Blanco *et al.* 1997).

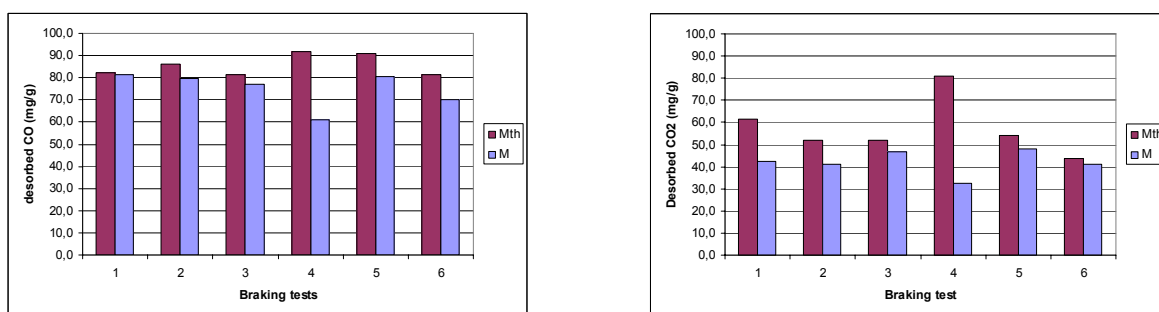


Figure 5. Amounts of carbon oxides released between 25 and 1200°C from material M and from material M_{th}. Abscissa: 1: 30strokes; 2: 30strokes bi; 3: 30strokes tri; 4: 100 strokes; 5: 100 strokes bi; 6: 100 strokes tri.

Another feature shown by Table 2 is that much more carbon oxides are released from debris samples than from the sawn material. This confirms the results recently published and discussed in terms of oxygen groups (Francois *et al.* 2007). However, these last results were obtained with debris samples issued from discs made of one material whereas the present work allows us to compare the results obtained with two differently graphitized C-C materials. Figure 5 shows such a comparison where it can be seen that the results are similar for both materials. This finding is in agreement with scanning electron microscopy observations which could not reveal clear morphological differences between debris issued from both materials. However, Figure 5 evidences that, for the same braking test, the amount of CO is systematically larger for material M_{th} than for material M. The consequence is that the mean value of the amount of desorbed CO for debris sample M_{th} (85.6 mg/g) is larger than that for debris M (75.0 mg/g). The same observation holds for the desorbed amounts of CO₂, with mean values of 57.4 and 42.0 mg/g for samples M_{th} and M, respectively. This may be related to the larger specific surface areas of the debris samples M_{th} (see Table 1). Nevertheless, it has to be kept in mind that oxygen groups would be better related to the surface of graphene rims than to the total surface area.

Finally, the preceding results support a mechanism of debris formation including the creation of reactive centres by rupture of the material under mechanical solicitations and the reaction of these centres with ambient oxygen and/or water vapour. It is quite difficult to interpret the slight differences between debris from both types of materials because the change in disc material likely induces changes in friction conditions, including the temperature of sliding surfaces.

Conclusion

Debris samples ejected -in the course of low temperature and high friction coefficient braking tests- from CVI-PAN brake discs made of materials with two different graphitisation degrees did not show large differences in their division state and physicochemical properties: They are highly divided, presenting specific surface areas around 200 m²/g, and are chemically quite different from the original materials, with an oxygen content reaching 10 wt%, approximately.

Nevertheless, the repetition of identical braking strokes series with periodically cleaned discs allowed us to achieve the production of samples with repeatable physicochemical properties. Thus, the following slight differences in debris properties could be evidenced:

- 1) Debris samples contain a small fraction of the original material, which can be detected by X-ray diffraction.
- 2) The specific surface areas of debris obtained from the graphitized material are, average, 60 m²/g larger than those obtained for debris from the non-graphitized material.
- 3) Debris samples issued from the graphitized material possess more oxygen groups, in particular carboxylic groups, than debris issued from the other material.

Acknowledgments

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References

- Blanco, C., Bermejo, J., Marsh, H., and Menendez, R. 1997. *Chemical and physical properties of carbon as related to brake performance*. *Wear* **213** (1-2):1-12.
- Chen, J. D., Chern Lin, J. H., and Ju, C. P. 1996. *Effect of humidity on the tribological behavior of carbon-carbon composites*. *Wear* **193** (1):38-47.
- delaPuente, G., Pis, J. J., Menendez, J. A., and Grange, P. 1997. *Thermal stability of oxygenated functions in activated carbons*. *J. Anal. Appl. Pyrolysis* **43** (2):125-138.
- Figueiredo, J. L., Pereira, M. F. R., Freitas, M. M. A., and Orfao, J. J. M. 1999. *Modification of the surface chemistry of activated carbons*. *Carbon* **37** (9):1379-1389.
- Francois, M., Joly, J. P., Kapsa, P., and Jacquemard, P. 2007. *A temperature-programmed desorption and oxidation investigation of wear debris from carbon/carbon composite aircraft brakes*. *Carbon* **45** (1):124-131.
- Gouider, M., Berthier, Y., Jacquemard, P., Rousseau, B., Bonnamy, S., and Estrade-Szwarczkopf, H. 2004. *Mass spectrometry during c/c composite friction: Carbon oxidation associated with high friction coefficient and high wear rate*. *Wear* **256** (11-12):1082-1087.
- Haydar, S., Moreno-Castilla, C., Ferro-Garcia, M. A., Carrasco-Marin, F., Rivera-Utrilla, J., Perrard, A., and Joly, J. P. 2000. *Regularities in the temperature-programmed desorption spectra of CO₂ and CO from activated carbons*. *Carbon* **38** (9):1297-1308.
- Peszynska-Bialczyk, K., Anderson, K. B., Szymanski, T., Krkoska, M., and Filip, P. 2007. *Thermal analysis of bulk carbon-carbon composite and friction products derived from it during simulated aircraft braking*. *Carbon* **45** (3):524-530.
- Szymanski, G. S., Karpinski, Z., Biniak, S., and Swiatkowski, A. 2002. *The effect of the gradual thermal decomposition of surface oxygen species on the chemical and catalytic properties of oxidized activated carbon*. *Carbon* **40** (14):2627-2639.
- Vix-Guterl, C., Dentzer, J., and Gadiou, R. 2005. *The importance of the carbon surface properties in carbon/ceramic composites*. *Annales de Chimie (Cachan, France)* **30** (6):593-608.
- Yen, B. K., and Ishihara, T. 1996a. *An investigation of friction and wear mechanisms of carbon-carbon composites in nitrogen and air at elevated temperatures*. *Carbon* **34** (4):489-498.
- Yen, B. K., and Ishihara, T. 1996b. *On temperature-dependent tribological regimes and oxidation of carbon-carbon composites up to 1800°C*. *Wear* **196** (1-2):254-262.
- Yen, B. K., Ishihara, T., and Yamamoto, I. 1997. *Influence of environment and temperature on "Dusting" Wear transitions of carbon-carbon composites*. *J. Mater. Sci.* **32** (3):681-686.