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STRUCTURE OF BRAKE PAD FRICTION FILMS ANALYZED BY GIXRD AND RAMAN SPECTROSCOPY[1]

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Abstract

The friction film formed between brake pads and vehicle cast iron discs during the braking process is a complex mixture of phases, coming from finely milled pad debris and from tribo-chemical reactions between disc/pad material and atmospheric oxygen. Depending on pad formulation and temperature, different phases form and different coefficients of friction will be obtained. However the third body is not homogeneous, but presents a layered structure. To understand the macroscopic consequences of this, further layer characterization with depth resolution is needed. In this study PMC pads that had been submitted to AK-Master braking test procedures against grey cast iron discs in a full scale dynamometer were analyzed using scanning electron microscopy, glancing incidence x-ray diffraction (GIXRD), and micro Raman mapping. The layered structure was inferred from the peak height evolution in GIXRD.
Keywords: Brakes; Polymer matrix composite; Third body.

ESTRUTURA DO FILME DE FRICÇÃO DE PASTILHAS DE FREIO ANALISADO POR GIXRD E ESPECTROSCOPIA RAMAN

Resumo

O filme de fricção formado durante o processo de frenagem entre a pastilha e o disco de ferro fundido do freio veicular consiste de uma complexa mistura de fases, proveniente do material da pastilha cominuída e das reações tribo-químicas que ocorrem entre o material do disco e da pastilha com oxigênio atmosférico. Dependendo da composição da pastilha e da temperatura, diferentes fases irão se formar e diferentes coeficientes de fricção serão obtidos. Porém o terceiro corpo não é homogêneo, mas apresenta uma estrutura em camadas. Para avaliar as consequências macroscópicas dessa estruturação, mais análises com resolução em profunidade são necessárias. Nesse estudo pastilhas PMC que foram submetidas a um ensaio AK-Master de frenagem contra discos de ferro fundido em um dinamômetro em escala, foram analisados com Microscopia Eletrônica de Varredura, Difração de Raios X com Ângulo Rasante (GIXRD) e mapeamento micro-Raman. A estrutura em camadas pode ser inferida a partir da evolução de intensidade dos picos na GIXRD.
Palavras-chave: Freios; Pastilhas poliméricas; Terceiro corpo.

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1 INTRODUCTION

Operating efficiency of dissipative brake systems depends on the interaction of grey cast iron discs with brake linings at their sliding contact interface. The interaction at the rubbing surface involves mechanical and chemical actions on a molecular level.(1)
The importance of investigating micro/nanotribological properties of surfaces and interfaces has long been recognized(2) and layers with ultra-fine microstructure different from that of the pad matrix have been described in friction couples.(3)
The friction film formed between brake pads and vehicle cast iron discs during the braking process is a complex mixture of phases, coming from finely milled pad debris and from tribo-chemical reactions between disc/pad material and atmospheric oxygen. Depending on temperature different phases form, giving rise to different coefficients of friction (COF).(4,5)

2 MATERIALS AND METHODS

Polymer Matrix Composite (PMC) pads of different formulations were submitted to brake test procedures against grey cast iron discs in a full scale dynamometer. Mainly around structural fibers (steel, copper, glass fiber) plateaus of milled debris and freshly formed phases developed on the pad surfaces.
Samples for microanalysis were cut from these rubbed areas. Backscattered electron images (BEI) and characteristic x-ray maps(6) were acquired using a scanning electron microscope (SEM Jeol LV5800) and an Energy Dispersive x-ray Spectrometer (EDS Thermo Noran). Micro Raman spectroscopy was performed in a home-assembled Raman spectrometer, where the sample was excited with a 30 mW He–Ne laser (Coherent), reduced to a 2 μm spot size with a 50× (achromatic) objective lens in an optical microscope (HD25 Zeiss Axiotech). After sample excitation the laser wavelength was rejected using a super-notch filter (Kaiser). Dispersion was achieved with a 500 mm spectrograph (Acton Research SP500i with a 600-g/mm grating) and spectra were collected with a liquid nitrogen refrigerated CCD camera (Princeton) LN/CCD-100EB) with back-illuminated detector.(7) Raman maps were compiled, obtaining 900 spectra per sample, on areas of 150 μm x 150 μm, with acquisition points 5 μm apart.
In order to be able to probe larger areas than with SEM and micro-Raman, glancing incidence x-ray diffraction (GIXRD) was used.(8) This technique probes around 1cm^2 on the sample surface and is therefore much more representative of the film composition than the micro-analytical Raman spectrometry. Using different incidence angles it is possible to probe surface layers of different thicknesses.

3 RESULTS AND DISCUSSION

Lateral distribution of elements and phases on rubbed PMC-pads was analyzed with SEM-EDX and showed a wide variety of elements distributed on the pad surface. Figure 1 shows an example of a BEI micrograph of a rubbed PMC pad and a composite element map of iron (red), barium (cyan), silicon (magenta) and carbon (green). On the BEI the friction film appears as light grey striated areas that correlate with iron rich areas on the map. Carbon can be seen mainly in the black areas of the BEI, but is also present throughout the friction film. Barium (from the pad raw material barite) appears mainly through gaps in the discontinuous friction film and the silicon signal is probably from a quartz grain, partially covered with magnetite.

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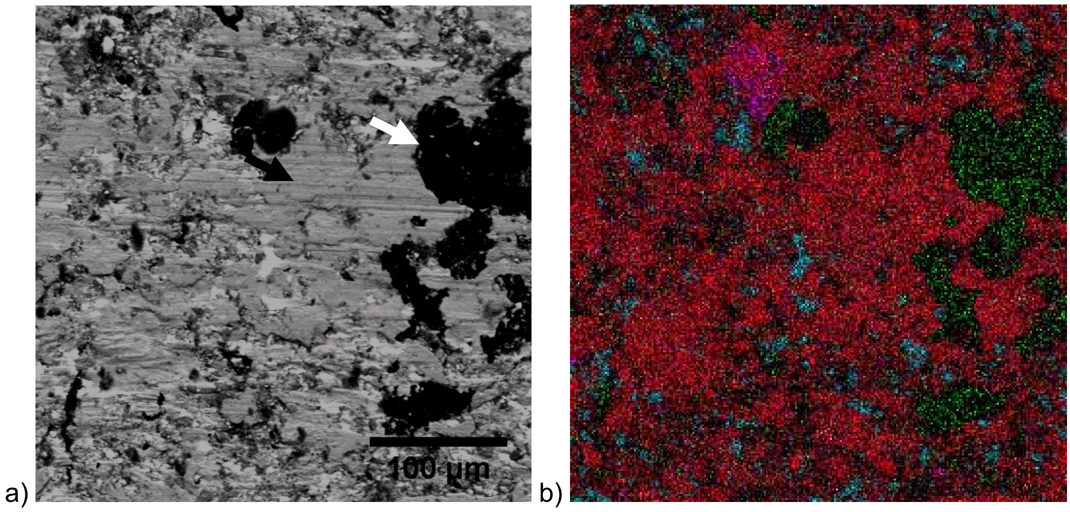

Figure 1. Friction film on a PMC pad; a) BEI, grey striated areas (black arrow) are the third body, dark contrasts indicate low Z elements (white arrow); b) composite map of selected elements (Fe red, C green, Ba cyan, Si magenta). Scale bar 100 µm.

Rubbed PMC pads were also analyzed with micro-Raman spectroscopy. A typical spectrum from the friction film is shown on Figure 2, where a magnetite peak and the D- and G- graphite bands can be seen.

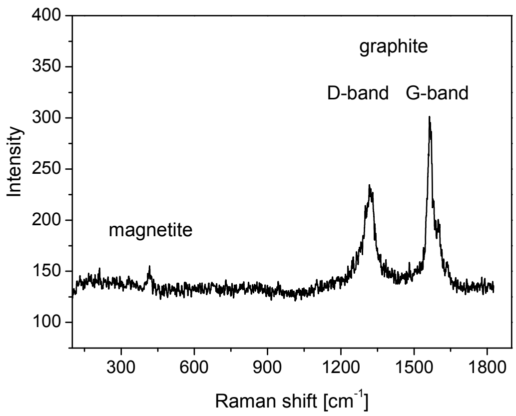

Figure 2. Typical micro-Raman spectrum from a friction film. Magnetite peak and graphite D- and G-bands are indicated.

Using the intensity of the graphite bands (between 1200 and 1600 cm^{-1}) and the magnetite peak (between 330 and 360 cm^{-1}) of 900 spectra, the phase maps of Figure 3 (b and c) were acquired. The approximate collection area is shown in Figure 3a (white square) on a BEI micrograph, where the lines burned by the laser during Raman spectrum acquisition can be recognized. Figure 3b shows the carbon peak intensity map, from 900 individual spectra, and Figure 3c the magnetite peak intensity map. Even with the low resolution of 30 x 30 pixel it can be seen that both phases were simultaneously present in some parts of the friction film. On some spots of the mapped area only graphite and on others only magnetite are present.

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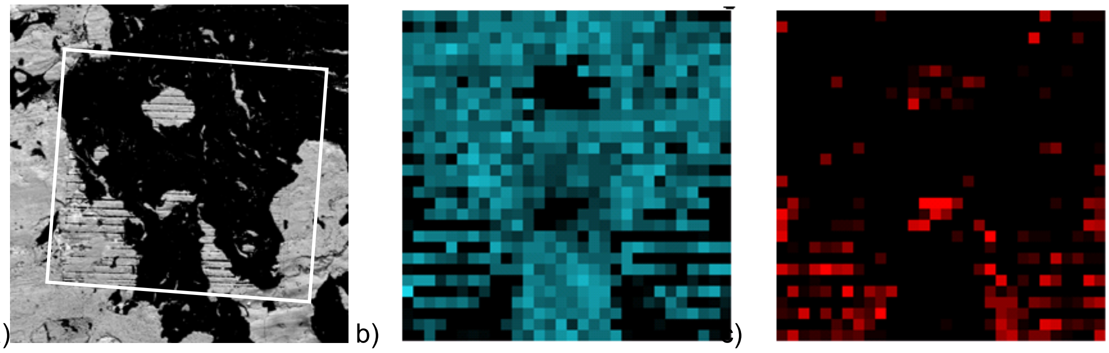

a) b) c)

Figure 3. a) BEI micrograph, b) low resolution (30 x 30 pixel) Raman graphite, and c) low resolution Raman magnetite map.

GIXRD using different incidence angles was utilized to reveal the layered structure of the friction films. To elucidate this procedure, Figure 4 shows the cumulative intensities of a specific diffraction peak (magnetite (311)) as a function of sample depth for different incidence angles in a magnetite surface film, calculated according to [8]. To estimate the thickness of the surface layer probed with a specific incidence angle, an accumulated intensity of 95% was chosen and the depth determined with a drop line on the intercept of the cumulative curve with the 95% line.

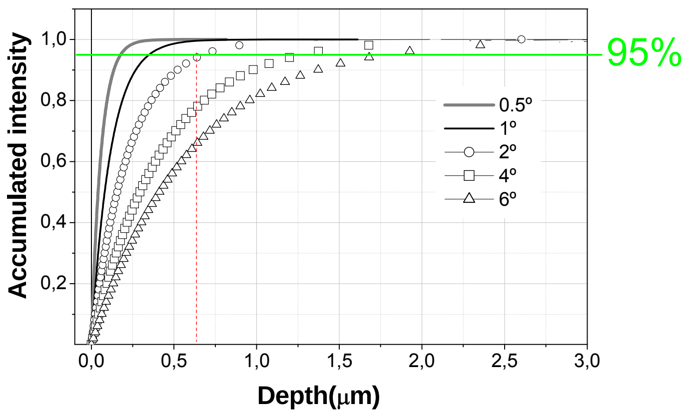

Figure 4. Cumulative diffracted intensity as a function of sample depth. The incidence angles are indicated on the image label. The intercept of the curves with the green 95% line indicates the probed sample depth, e.g. the red drop line on the intercept with the 2º line indicates a probed thickness of 0.7 µm when measuring with 2º incidence).

It was observed that different phases were present in the layers when monitoring increasing depths of several sample surfaces. On Figure 5a, the shallowest pattern with 0.5º incidence angle (penetration of 0.2 µm) showed a single peak corresponding to strongly textured graphite, oriented parallel to the surface. Graphite grain size in this friction film, calculated with the Scherrer formula, was around 15 nm. The 1º diffractogram that corresponds to a sampling depth of 0.3 µm, revealed the presence of magnetite and barite, while at 5º (more then 1.5 µm x-ray penetration) the full phase composition of the PMC pad contributes to innumerous diffraction peaks.

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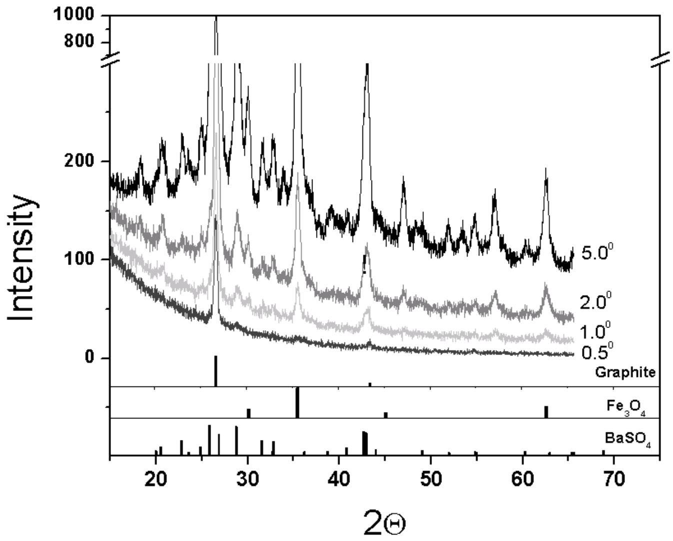

Figure 5. GIXRD patterns of PMC pad, showing different peaks for different penetration depths. Peaks of most important phases are indicated below.

In Figure 6 several phases can be recognized in the most superficial layer. In this 3D graph the continuous increase of the graphite peak (at ~26º, red arrow) was observed, while the barite doublet (at ~43º, white arrow) increased until 2º incidence angle and afterwards decreased. The increase indicated that graphite was equally distributed in the upper ~2 μm. The fact that the relative intensity of the barite peak decreased indicates that barite was enriched in the upper ~1μm.

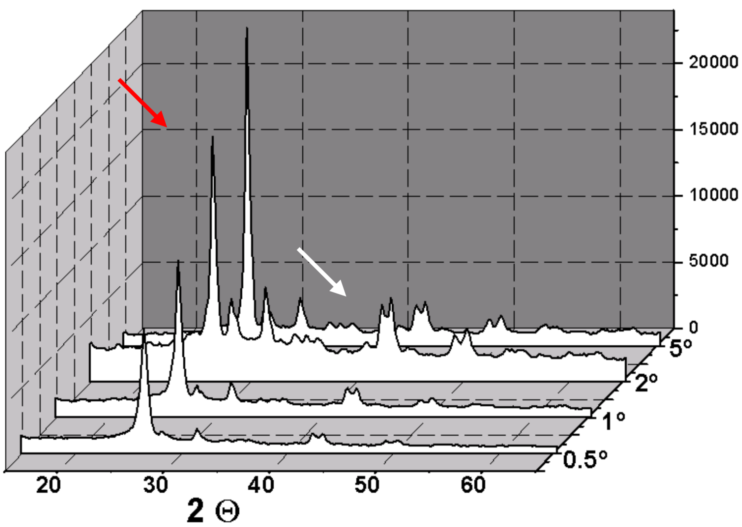

Figure 6. GIXRD patterns of PMC pad, showing different depth evolution of graphite (red arrow) and barite (white arrow).

4 CONCLUSIONS

The complexity of the friction film formed on braking couples in vehicular brake applications that use PMC-pads against cast iron discs makes it necessary to use different analytical techniques to asses the consequences of phase composition and layered structure of the friction layers on the coefficient of friction (COF) and the noise. A pure graphite layer on the surface correlates with low COF and low noise, but too much graphite induces failure of the brakes (fading), and has to be avoided.

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On the other hand, too much barite would induce noise (vibration), due to fluctuations in the COF. Further studies that correlate COF and micro-analytical phase studies are required.

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