MAGNETITE FORMATION OBSERVED WITH TEM ON BRAKE DISCS

Ruth Hinrichs[1]; Marcos Antonio Zen Vasconcellos[2]; Werner Oesterle[3]; Claudia Prietzel[4];

The most common brakes utilized in automotive braking are polymer matrix composite (PMC) pads that are rubbed against cast iron discs. During the braking process reactions take place and the new phases, mixed with wear debris, adhere to the surfaces forming a third body. Brakes tested with an AK-Master protocol developed a magnetite layer between the interacting surfaces. Disc samples that reached high temperatures (650℃) in the test procedure were prepared with Focused Ion Beam (FIB). Energy Filtered Transmission Electron Microscopy (EFTEM) results revealed that magnetite was formed on the interface next to graphite flakes in the cast iron disc. TEM captured the detachment of nanometer sized iron particles from the matrix due to the wedging in of graphite layers. Nano-sized cracks between particles allowed the access of oxygen and the formation of magnetite. The graphite from the disc was amorphized during the process.

Keywords: tribology, polymer matrix composite, magnetite

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[1]Associate Professor, Geology Department, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil
[2]Associate Professor, Physics Department, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil
[3] Permanent Researcher, Bundesanstalt für Materialforschung und -prüfung, BAM-V.1 WG ”Nanocharacterization of Materials”, Berlin, Germany
[4] Researcher, Bundesanstalt für Materialforschung und -prüfung, BAM-V.1 WG ”Nanocharacterization of Materials”, Berlin, Germany

INTRODUCTION

Despite many polymer matrix composite (PMC) brake pad formulations [1-6], the main component of the friction film (“third body”) formed during braking, when sliding the pad against a cast iron disc, is magnetite [2-6]. The formation of this iron oxide occurs already in the initial low temperature phase of the friction tests, as can be shown with debris coming from early burnishing stages of the brake [7], making one wonder how the process happens so fast. Other authors identify magnetite in friction experiments only above 400 ºC [8], even though the main magnetite peak is present in their lower temperature XRD patterns.

The cast iron disc contributes to the magnetite formation not only as an abundant iron source. Images obtained with an EFTEM showed that the graphite flakes in the cast iron matrix play an important role in the process.

MATERIALS AND METHODS

PMC pads with approximate composition shown in Table 1 were submitted to a complete AK-Master testing procedure against a grey cast iron disc in a full scale dynamometer, reaching temperatures of 650 ºC on the braking interface.

rubber	binder	fiber	metals	filler
0 – 3	5 - 7	2 - 10	15 - 20	40 - 50

Table 1: volume % content of the PMC pad

The cast iron disc counterpart, covered with a bluish surface film, was examined with Scanning Electron Microscopy (Jeol JSEM LV5800). A surface spot was selected to prepare a TEM-lamella, using a Focused Ion Beam instrument (FIB-FEI), with 30 keV Ga ions to machine a 20 micrometer long, 10 micron wide and 100 nm thick lamella. To preserve the friction film on the top surface, a platinum strip was deposited beforehand. The sample was soldered on an Omniprobe copper sample holder and examined in a Transmission Electron Microscope (Jeol JEM2200FS), equipped with a 200kV FEG, Scanning Transmission Electron Microscopy detector (STEM), Ω-filter for Energy Filtered Transmission Electron Microscopy (EFTEM), and Energy Dispersive X-ray detector (EDX). Elementar maps were acquired either by STEM-EDX or using the three window method in EFTEM [9,10].

RESULTS AND DISCUSSION

Figure 1a shows the microstructure of a pristine grey cast iron disc, in a backscattered electron micrograph. Abundant graphite flakes (black) with an uniform distribution and random orientation can be seen in the ferritic/pearlitic matrix (light grey). Figure 1b shows a backscattered electron image of the cast iron disc after the AK-Master friction test. The graphite flakes and the iron matrix are now partially covered with a dark grey film. Additional XRD from the film showed that it is composed mainly of magnetite, minor hematite, and possibly pyrite.

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a) b)

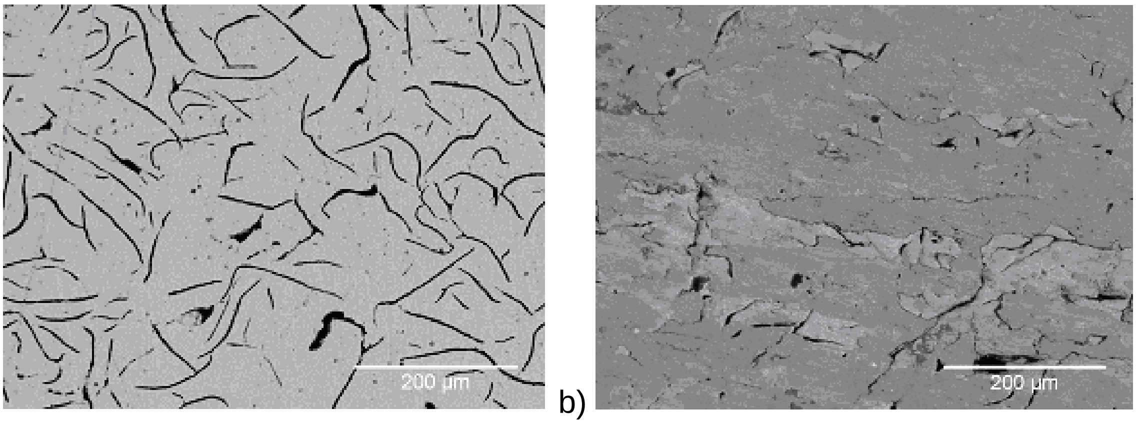

Figure1: a) Backscattered electron image of a pristine grey cast iron surface with graphite flakes (black) in a ferritic/pearlitic matrix (light grey); scale bar 200 μm;
b) surface of the cast iron disc after the AK-Master friction test. The graphite flakes and the iron matrix are partially covered with a dark grey film; scale bar 200 μm.

A cross sectional cut from the friction film was prepared with a FIB for TEM inspection. In an optical microscope, the worn disc surface showed a bluish luster and the spot selected for the FIB cut happened to be on top of a graphite flake ending on the disc surface under the magnetite film. A Ga-ion induced secondary electron image of the lamella, still attached to the disc, is shown on Fig.2a. Afterwards the lamella was lifted of the sample and soldered to a copper Omniprobe sample holder, as can be seen in the optical micrograph in Fig. 2b (sample in position "B").

a) b)

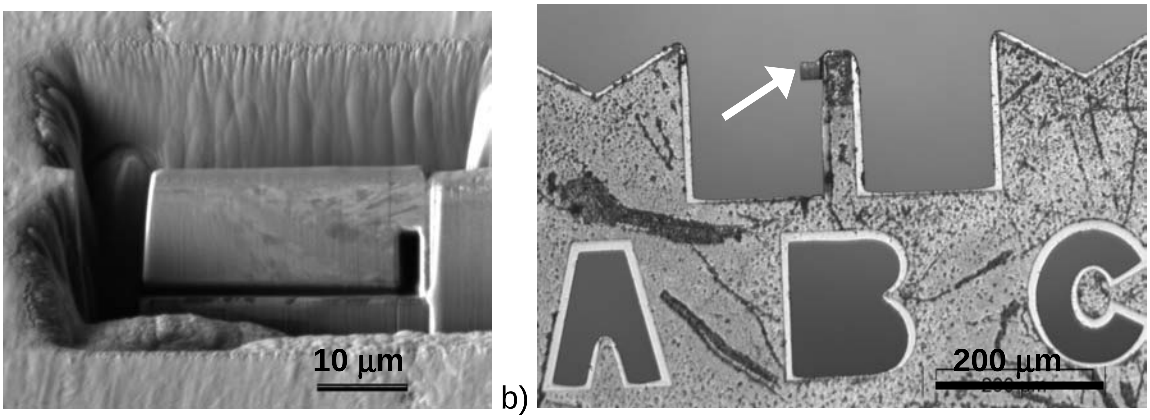

Figure 2: a) Ion-induced secondary electron image of the FIB cut of a TEM lamella still attached to the disc surface. Scale bar 10 μm; b) Optical micrograph of the sample soldered to a copper sample holder in position "B" (white arrow). Scale bar 200 μm.

The STEM image in Fig.3a shows the intercept of the graphite flake with the disc surface and the overlying magnetite friction layer. The STEM-EDX composite map (Fig. 3b) shows carbon (green), iron (red) and oxygen (blue). At this magnification the top layer seems to consist completely of iron oxide (blue + red = purple). At the boundaries of the graphite, iron oxide seams (purple) are observable, and minute iron particles (red) that were detached from the iron borders.

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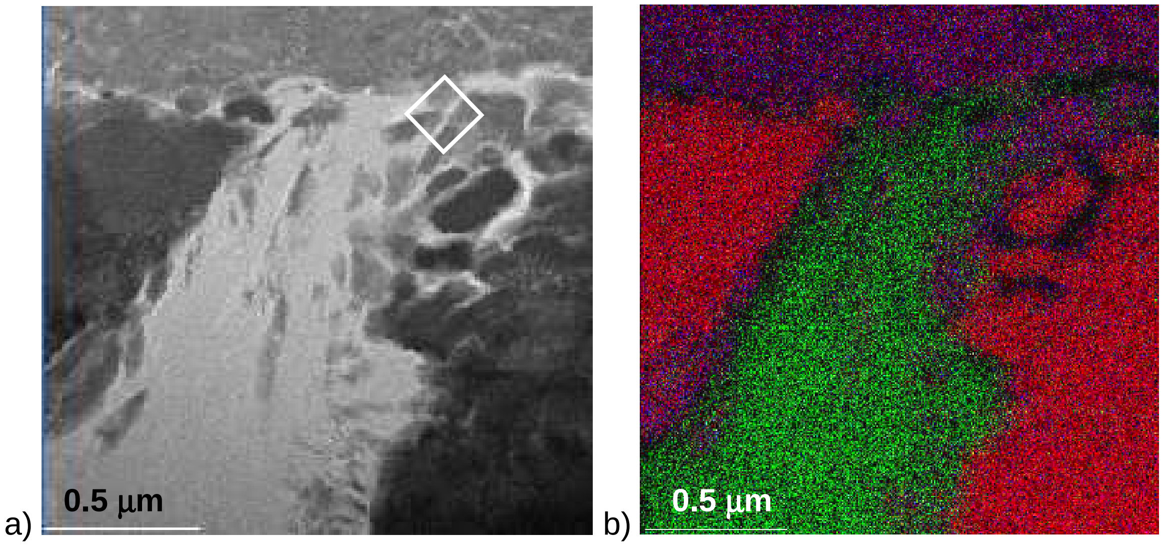


Figure 3: a) STEM micrograph (scale bar 0.5 μm.) showing the boundary between the magnetite layer on top, and the cast iron surface with a graphite flake diagonally crossing the iron bulk. The tilted white square indicates the region of the higher magnification EFTEM image in Fig. 5; b) STEM-EDX composite map shows carbon (green), iron (red) and oxygen (blue). The purple regions on top and at the red-green boundaries are iron oxide.

The EFTEM micrograph (Fig. 4 a) magnifies a region in the friction film. Small iron grains (at the right hand side of the image) are located next to a more electron-transparent material that is layered with even lighter matter. The zero-loss image in Fig. 4b) shows a magnification of the area indicated with a square in Fig. 4a). Fig. 4 c) is an EFTEM elementar composite map (iron, carbon and oxygen) of the area in Fig. 4b), showing that the layer is formed of magnetite nano-particles (purple) interspersed with carbonaceous material (green).

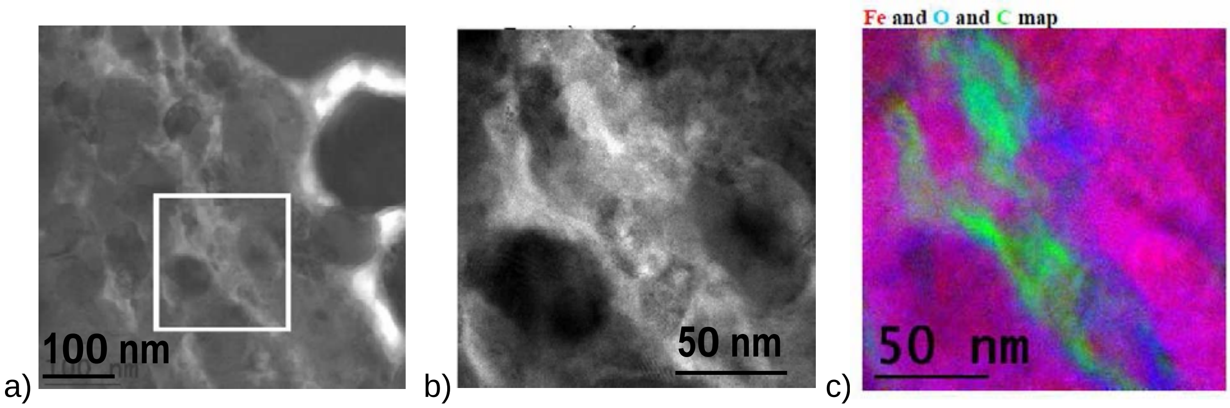
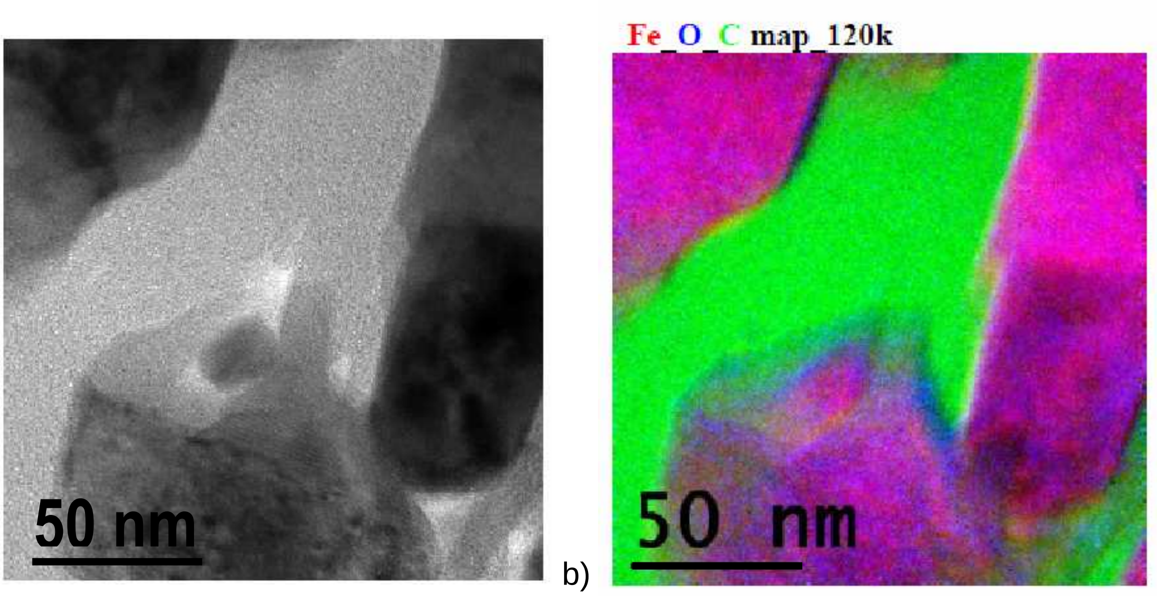


Figure 4: a) EFTEM micrograph of the friction film, scale bar 100 nm; b) higher magnification zero-loss image of the square indicated in 4a; scale bar 50 nm; c) EFTEM composite elementar map (iron: red, carbon: green, oxygen: blue) of the same area as 4b; scale bar 50 nm.

Fig. 5a) shows a high resolution zero-loss electron micrograph of the white tilted square in Fig. 3a). The composite elementar map in Fig. 5b) was obtained with the EFTEM and is composed of iron (red), graphite (green) and oxygen (blue). The pink color is from the superposition of red and blue, revealing the presence of iron oxide. Details of the graphite-magnetite interface can be observed, disclosing the mechanical action of graphite. The graphene layers of the graphite flakes detach form each other under mechanical shear stress due to the pressure exerted during the friction test, and are wedged into the iron bulk chipping off nanometer sized iron particles. Cracks due to the different compressibility of graphite and iron [11] provide access of oxygen to the large amount of freshly formed surface sites enabling fast oxidation of iron into magnetite.



a) b)

Figure5: a) High resolution EFTEM micrograph of the area indicated with a white tilted square in Fig. 3a; b) EFTEM composite elementar map (iron: red, carbon: green, oxygen: blue) of the same area. Scale bar for both images 50 nm.

CONCLUSION

FIB and EFTEM proved to be a powerful tool to capture the process of ongoing tribo-oxidation, revealing that the reaction is fostered by the compression and the shear stress exerted on the grey cast iron. The high anisotropy of elastic constants in the graphite crystalline structure causes delaminating of graphene layers that penetrate the iron bulk, to chip off iron nanoparticles, producing high surface to volume ratio. Microcracking of the disc happens due to the differences in elastic moduli of iron and graphite and allows the access of enough oxygen to the freshly formed surface sites to rapidly form magnetite.

ACKNOWLEDGEMENTS

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