

## NANOPARTICLES FROM BRAKE PADS WEAR

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### Abstract

Exposure to particulate air pollution has been associated with a variety of health problems. One of the main sources of metal-rich airborne particulate pollution in roadside environments are brake-wear emissions. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM), Mössbauer spectroscopy (MS), X-ray powder diffraction (XRD) was used to make a quantitative evaluation of wear particles in two samples. Sizes, morphologies, oxidation state, and trace element compositions of wear particles were investigated using a combination of several methods revealed high concentrations of Fe species and phases, often associated with carbonaceous material. SEM and TEM observations show that brake wear particles with a size of tens to hundreds of nm mainly form particle agglomerates. However, ultrafine (<100 nm) particles are likely to pose a health threat after inhalation and/or ingestion.

**Keywords:** Wear particles, analysis, TEM, iron oxides, metallic particles

### 1. INTRODUCTION

Exposure to airborne particulate matter (PM) has been related to some health problems. In particular, exposure to fine (2.5–0.1  $\mu\text{m}$ ) and ultrafine (<0.1  $\mu\text{m}$ ) particles is associated with deterioration of cardiovascular and neurological health or impaired pulmonary [1,2]. The airborne PM suspended in air can be of both natural and anthropogenic origin. Anthropogenic PM reaches the atmosphere due to industrial activity, heating and automobile traffic. The brake emissions account for one of the major sources of airborne ultrafine particles (UFP) in the roadside environment [3,4]. Some works [5,6] reported that brake wear PM contributes to the total PM<sub>10</sub> mass by approximately 11 %–21 %.

The iron is the dominant metal in brake-wear particles. Iron chips and/or Fe-containing compounds are one of the many components that brake pads commonly contain [7,8]. However, wear particles are released from the brake pads and at the same time from the brake disc made from cast iron. This is the reason, why Fe-bearing particles often constitute about 50 % of the total mass of particles emitted from brake systems [9]. The various forms of iron including oxides or hydroxides, carbides and/or metallic Fe ( $\alpha\text{-Fe}$ ) can be found in Fe-bearing particles in brake emissions. The knowledge of the oxidation state of Fe, particle size distribution and concentration of each Fe-phase may be particularly important [10] in the context of human health hazard as well as a potential association with neurodegeneration and Alzheimer's disease.

From the point of view of studies dealing with braking emissions and the composition of wear particles, we can find two main directions of research. Part of the works is focused on studying the effects of braking conditions on PM production [11]. Others are focusing on particles in the air in the context of selected localities or population groups [12,13]. In our study we use a combination of scanning (SEM) and transmission (TEM) electron microscopy together with X-ray powder diffraction and Mössbauer spectroscopy analysis to obtain chemical and phase composition and morphology of wear particles from automotive brake systems.

## 2. MATERIALS AND METHODS

Wear particles (debris) were collected by sweeping brake pads obtained from passenger car services. Two samples of wear debris, labelled as F and R, were analysed using combinations of analytical and microscopic techniques.

A TESCAN LYRA 3XMU FEG/SEM scanning electron microscope equipped with an XMax80 Oxford Instruments detector for energy dispersive X-ray analysis (EDX) was used to follow the chemical composition. For the SEM study, the wear particles were captured to an aluminum stub by a double-sided sticky carbon tape. The secondary electron (SE) images and energy dispersive X-ray spectra (EDS) were obtained at 12 kV and 15 kV accelerating voltage, respectively.

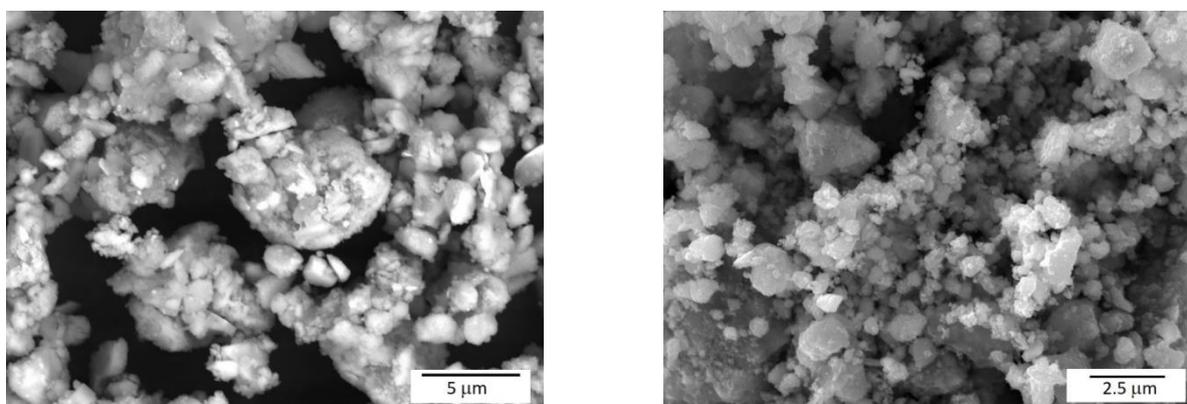
A Jeol JEM 2100F HRTEM with a Schottky cathode operating at 200 kV was applied for study the finest fraction of wear particles. For the TEM study, part of samples was placed in a 1.5 ml Eppendorf tube filled with 1 ml pure ethanol, and mix for 2 minutes. Then a drop of the finest fraction was placed onto a copper TEM grid coated with a lacey carbon film and left to dry. The conventional TEM mode were used for bright-field (BF) images, scanning transmission (STEM) mode were applied for high-angle annular dark-field (HAADF) images and EDS elemental maps.

The phase compositions studies were carried out with Empyrean diffractometer (Panalytical) in the Bragg-Brentano geometry with  $\text{CoK}\alpha$  radiation ( $\lambda = 0.17902$  nm) at room temperature (RT). The analysis of patterns was realized by HighScore® software and the ICDD (PanAnalytical) database.

The  $^{57}\text{Fe}$  Mössbauer measurements were carried out at RT using a  $^{57}\text{Co}(\text{Rh})$  source in transmission geometry with detection of 14.4 keV gamma radiation (MS) using a standard Mössbauer spectrometer. A pure  $\alpha$ -Fe foil was used as a calibration standard for the velocity scale. The computer processing of the spectra was done using CONFIT program package [14].

## 3. RESULTS AND DISCUSSION

The scanning (SEM) and transmission (TEM) electron microscopy were used to obtain independent information on the composition, structure, morphology and particle size of the brake-wear particles. Overview of prevalent size of brake-wear particles shows SEM image on **Figure 1**. The main fraction of wear particles was around 1  $\mu\text{m}$  in size. The larger, sharp-edged particles were also observed in both samples. Agglomerates composed of different sizes particles were noted.

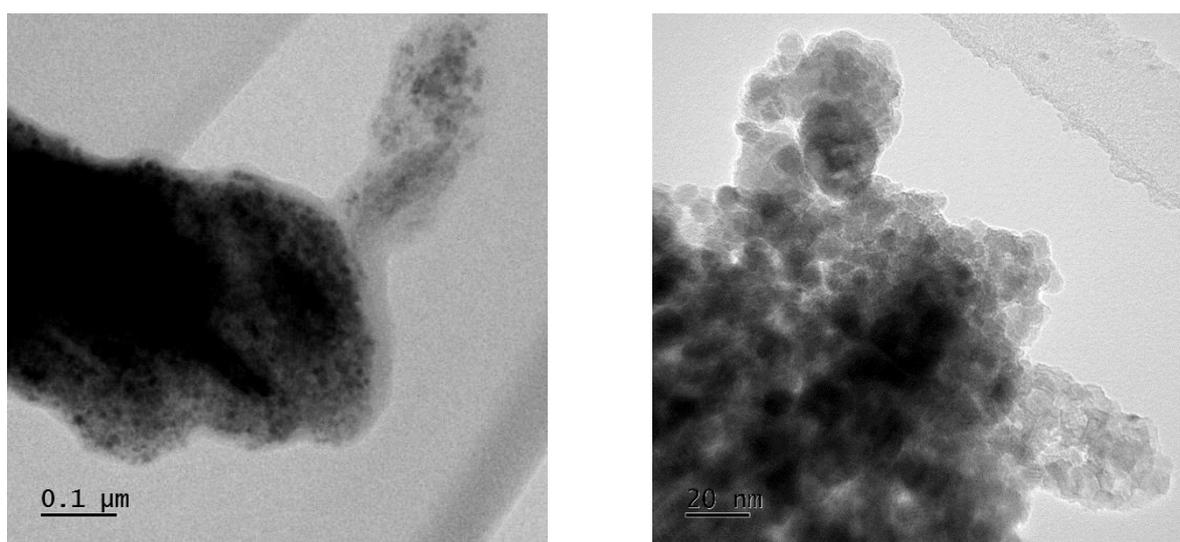


**Figure 1** SEM images of brake wear particles obtained from sample F(left) and R (right)

All particles, agglomerates but also larger grains, have similar elemental composition typical of brake emissions. The dominant elements are Fe, C and O, and Cu, Al, Si, S, Mg, Mn, Zn, and Ca are present to a lesser extent. According to EDX analysis is possible to say that the wear particles predominantly contain iron.

The TEM images show that the agglomerates comprise prolific numbers of particles ~10 nm in size (**Figure 2**, right). The elemental analysis using EDX in STEM mode showed the presence of Fe, O and C, with lower concentration of other elements analogous to result SEM/EDX analysis. However, the distribution of these minor elements is not uniform throughout the agglomerates. The influence of the original material of the brake pads is also evident, when the composition of samples F and R were different. The finest fraction of brake products from sample F contain carbon structures with some degree of crystallographic order (**Figure 2**, left). Interplanar distances of this carbon structures are approximately 3.3 Å, similar structures observed Gonet [15] in agglomerates of ultrafine brake-wear particles. Nanoparticles were trapped in the carbon structure.

Compared to that only agglomerates of nanoparticles without any carbon matrix were observed on sample R (**Figure 2**, right). High concentration of carbon in the form carbon matrix (sample F) can be probably connected with type of resin used for production of this brake pads.



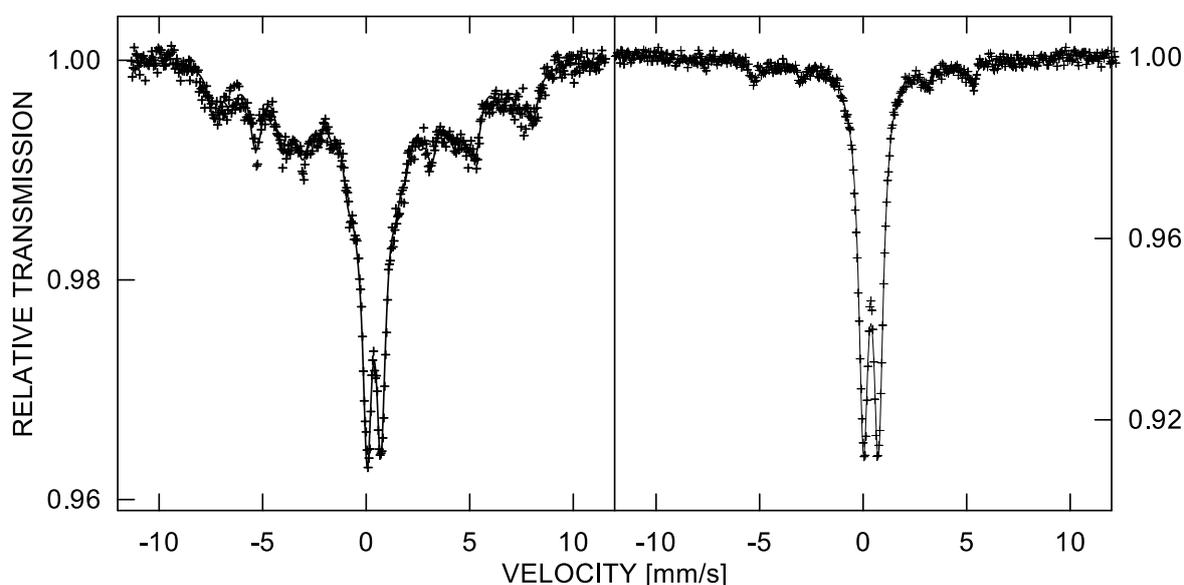
**Figure 2** TEM images of brake wear particles. Matrix with trapped nanoparticles in sample F (left) and detail of agglomerate found in sample R (right).

**Table 1** The phases composition of wear particles (weight percent) according XRD measurements.

Phase	Formula	Sample	
		R	F
Hematite	$\text{Fe}_2\text{O}_3$	46	52
Goethite	$\text{FeO} \cdot (\text{OH})$		22
Magnesium diiron (III) diiodide	$(\text{MgFe}_2)\text{O}_4$	42	
Iron / ferite	$\alpha\text{-Fe}$		11
Manganese iron carbide	$(\text{Mn}_4\text{Fe}_3)\text{C}_3$	8	
Iron (II) Iron (III) aluminium hydroxide sulfate hydrate	$\text{Fe}_2(\text{Fe}_{0.76}\text{Al}_{0.24}) \cdot (\text{OH})_6(\text{SO}_4)_{0.5}(\text{H}_2\text{O})_{2.4}$	2	
Chalcopyrite	$\text{CuFeS}_2$		1
Zhanghengite	$\text{CuZn}$		1
Quartz low	$\text{SiO}_2$		13
Calcite	$\text{CaCO}_3$	1	
Carbon / graphite	$\text{C}$	1	

The phase composition of wear particles samples determined by XRD shows that the wear particles contain 80 or more weight percentage of iron-containing compounds. Various iron oxides and iron hydroxides had been noted. The phase composition of wear particles samples is present in **Table 1**. Our previous study [7] was targeted the possible pollution caused by brake pads. The brake disc was determined as a source of the most of particles. The iron oxides, hydroxides and carbides are product of friction and thermal interaction of brake pads and mainly disks. On the contrary, the other minerals, sulphides and carbon, come from brake pads.

Due to high iron content the Mössbauer spectroscopy (MS) was used for more detailed identification of wear particles. Spectra analysis yields the relative contents of individual Fe-containing phases in atomic fraction of iron (A) and corresponding hyperfine parameters of phases: isomer shift (IS), quadrupole shift ( $Q_{sh}$ ) and quadrupole splitting ( $QS_{pl}$ ), and hyperfine induction ( $B_{hf}$ ). In view of the fact the similar content of individual iron phases, spectra of the same appearance were expected. As the main component of the spectra, a doublet representing the paramagnetic phase was present in both samples (**Figure 3**) [16]. In the sample F comprises was contents of paramagnetic phase in atomic fraction of iron atom equal 1. The spectrum was constituted only by doublet. Compared to that in the spectra of R sample minor sextets can be observed, except dominant doublet.



**Figure 3** Mössbauer spectrum of the sample R (left) and sample F (right).

The several groups were identified on the basis of corresponding hyperfine parameters for components and attributed to the following phases: (i) Fe based oxides particles with magnetic splitting, (ii) metallic particles of iron, (iii) iron carbon  $Fe_3C$ , and (iv) paramagnetic particles. Their contents are reported in **Table 2**.

**Table 2** Mössbauer spectroscopy results; Contents of phase groups in atomic fraction of iron atoms for samples measured at RT.

Sample	Fe based oxides	Fe	Iron carbon	Paramagnetic particles
R	0.37	0.16	0.10	0.37
F				1.0

A combination of MS, XRD and TEM results demonstrated that the paramagnetic fraction can be attributed to the presence of fine nanocrystalline particles ( $\leq 10$  nm). The composition of paramagnetic particles of sample F according to the next MS experiments roughly corresponds with phases observed by MS in the sample R.

The iron-bearing particles containing metallic iron and iron carbides that originate from interaction brake pads with brake disc made from cast iron.

#### 4. CONCLUSION

The wear particles originating from brake pads have been studied using a combination of scanning electron microscopy (SEM) and transmission electron microscopy (TEM), Mössbauer spectroscopy (MS), X-ray powder diffraction (XRD). Wear particles are mainly formed by various iron oxides and hydroxides. Based on MS experiments, the presence of the following phases can be defined: (i) Fe-based oxide particles with magnetic cleavage, (ii) metallic iron particles, (iii) iron carbon  $\text{Fe}_3\text{C}$  and (iv) paramagnetic particles. The paramagnetic fraction observed during MS experiments at RT corresponding with presence of fine nanocrystalline particles ( $\leq 10$  nm). The expected particle size in the nm range was confirmed by the TEM results.

Based on current knowledge, it is possible to say that emissions of particles generated by the wear of brake pads/discs can be probably influenced by adjusting the composition of the brake pads. However, great care is needed so that these modifications do not lead to an even greater threat to health and environment.

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