ANALYSIS OF NANOPARTICLES RELEASED FROM THE CAR BRAKES

ŠVÁBENSKÁ Eva[1], ROUPCOVÁ Pavla[1], SCHNEEWEISS Oldřich[1,2]

[1]Institute of Physics of Materials AS CR, Brno, Czech Republic, EU

[2] Central European Institute of Technology & Institute of Physics of Materials (CEITEC IPM), Academy of Sciences of the Czech Republic, Žižkova 22, 61662 Brno, Czech Republic, EU

Abstract

Our research is focused on the phase, structure and chemical analysis of the powder particles released by braking of cars from their brake components – discs and pads. The basic information on structure and phase composition was obtained by X-Ray Powder Diffraction, Mössbauer Spectroscopy and scanning electron microscopy with EDX. The results of the particle analysis are compared with materials used for manufacturing brake components and with the powder prepared by ball milling of the mixture of the pad composite and disk steel. Most of recognized nanoparticles are based on carbon, silica/silicates and iron oxides. Their effects on street environment are mentioned.

Keywords: nanoparticles, wear debris, automotive brake

1. INTRODUCTION

An important source of airborne particles is road traffic negatively influencing human health as reported in recently published papers [1, 2]. Among the sources of the dust in on roads belong emitted particles from the brake components [3, 4]. Proportion of wear brake emissions to non-exhaust traffic PM10 emissions is between to 16 - 55 by mass [5]. Plenty of different type of particles can be emit during the breaking. Brake disc are predominantly manufactured from a cast steel. On the other hand brake pads materials are composed of wide range of component, e.g. fibres, abrasives, lubricant, fillers and binders [6]. The chemical composition of commercial brake lining depends on the type of pads and their producers. Various approaching to the study of wear debris was described in literature, e.g. collecting debris in real condition [7], preparation of debris by brake dynamometer experiments [8, 9], or by ball-milling of materials [10]. Each of this method has some limitation. Sample from real condition probably contain also other particles from road, exhaust fumes and surrounding of sampling point. A brake dynamometer experiment does not take account of effect on humidity, road salt or dust on the road. Ball-milling produces quite different type of debris to comparison with dynamometer experiments [10]. It can be cause different wear abrasion, temperature of brake, hydraulic press, surrounding condition, etc. during formation and emission of debris. For example phenol–formaldehyde resin, which contents are 20-40% in the pad materials, transforms at temperature above 300°C [11] which is temperature of wearing brake components during breaking process [12].

In the present paper we report our results of study of the phase, structure and chemical analysis of the surfaces of disks and pads and powder particles, namely nanoparticles, taken from their surfaces. The results of the particle analysis are compared with materials used for manufacturing brake components and the powders prepared by ball milling of the mixture of the pad composite and the disk steel.

2. MATERIALS AND METHODS

Sample of debris were collected/prepared from worn in ventilated brake disc and pads from one of the most common personal car in Czech Republic. Grinding and polishing surface of brake disc and pads were investigated by optical microscope (Neophot 32 by Carl Zeiss Jena) and scanning electron microscope JEOL 6460 with Oxford Instruments analytical equipment INCA Energy (EDX).

Chips of the brake disc and pad were milled in the planetar ball-mill (Pulverisette 7) after define time. The dry milling was carried out in air filled container with volume 0.5dm^3. During milling process the temperature of balls and powder increase roughly above 100°C and decreased fast to room temperature after the milling was stopped.

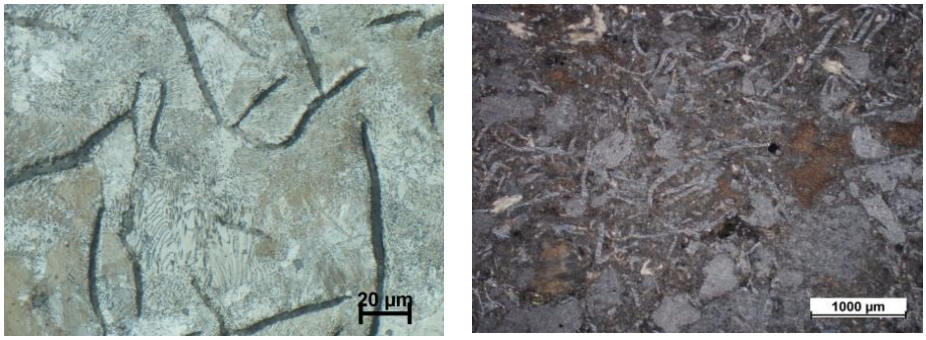
The X-ray powder patterns (XRD) were collected on X'Pert diffractometer and CoKα radiation with qualitative analysis by HighScore® software and the JCPDS PDF-4 database. For a quantitative analysis HighScore plus® with Rietveld structural models based on the ICSD database was applied.

^{57}Fe Mössbauer spectroscopy was carried out in scattering geometry with detection of 14.4 keV gamma radiation (MS) and conversion electrons (CEMS). The spectra were measured at room temperature and calibrated against α-Fe. The computer processing of the spectra was done using CONFIT program package [13].

3. RESULTS AND DISCUSSION

The results of surface structure observations obtained using OM and SEM are shown in Fig. 1. The disc sample shows pearlitic structure which is typical for cast steels and the pad surface corresponds to a complex mixture of materials.

XRD analysis showed variation at phase composition worn in part of brake disc (BK-B) and area of disc, which was not affect friction (BK-U). Samples BK-B contain 92% wt α-Fe, 3.5% wt cementite and 4% wt graphite and similar composition (85.5% wt α-Fe, 6% wt cementite and 8.5% wt graphite) were observed for sample BK-U. Higher concentrations of cementite and graphite were due to fact, that sample BK-U was bulk material of brake disc and it was not affect friction.



A **B**

Fig. 1 Image from light optical microscope - pearlitic structure of brake disc -1000x, etched by 2% Nital (A) and brake pads - 25x (B).

The XRD analysis of brake pads show presence of α-Fe, barite $BaSO_4$, corundum Al_2O_3, pyrite FeS_2, graphite C, calcite $CaCO_3$, fluorite CaF_2, mullite $Al_6Si_2O_{13}$, wustite FeO and magnetite Fe_3O_4. However, this list is not a complete, common brake lining includes more then 20 items from very large group of compounds (nearly 700) use for brake lining manufacturing [14]. Also phenolic resin used as binder in pads (its amount can be about 20-40%) was not detected by our measurements of XRD diffractions.

Wear debris was collected by sweeping of the surface of brake pads and brake disc. Its XRD diffraction sheets in Fig. 2 and Mössbauer spectrum are shown in Fig. 3. The X-ray measurement collected on the sweeping debris in Fig. 2 (bottom) contains mainly the graphite and quartz. The graphite and minor phases (iron, pyrite, calcite, iron oxides, minerals etc.) originate from brake pads, but the quartz is from outside. Its amount, crystallite size and morphology does not match the silica from the pads material. In the Mössbauer spectrum (where iron containing phases are detected only) were recognized following phases: iron oxides

(Fe^{2+} and Fe^{3+}) alpha iron, and iron carbide (~cementite). For the comparison the spectrum of the powder sample prepared by ball milling of the brake pad and brake disc materials for 14 hrs is shown also in Fig. 3 (bottom). The alpha iron phase dominates there besides the paramagnetic Fe^{3+} and an amorphous phase. Formation of the amorphous phase is probably results of severe plastic deformation during the ball milling process. The existence of amorphous (not well crystalline, not long range order) parts is reported as well by XRD in Fig 2 (top). The peaks of iron, graphite, calcite, etc. are broadening whit the milling time. The pyrite is the single phase not influenced by milling.

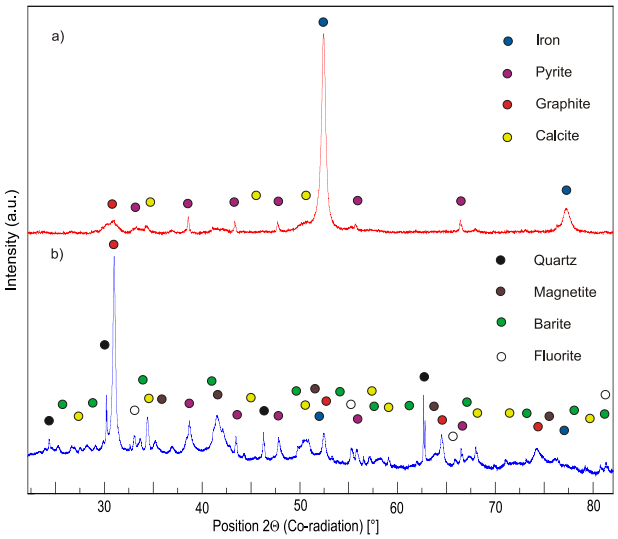


Fig. 2 Top: XRD pattern of the powder sample prepared by ball milling of the brake pad and brake disc materials for 14 hrs. Bottom: XRD pattern of the powder sample obtained by sweeping of the surface of brake pads and brake disc.

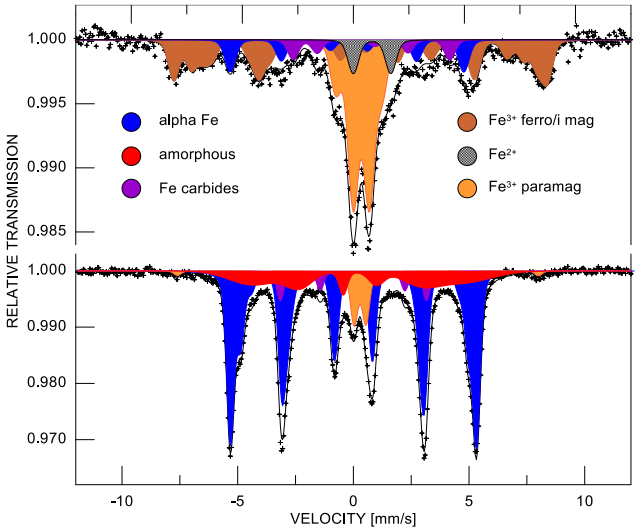


Fig. 3 Top: Mossbauer spectrum of the powder sample obtained by sweeping of the surface of brake pads and brake disc. Bottom: Mossbauer spectrum of the powder sample prepared by ball milling of the brake pad and brake disc materials for 14 hrs.

Mossbauer spectra of the brake disc and brake pad taken in scattering geometry with detection of 14.4 keV gamma radiation (scanning depth up to ~30 micrometers) and with detection of conversion electrons (CEMS with scanning depth up to 200 nanometers) are drawn in Figs. 4 and 5. They show that paramagnetic iron carbide dominates in the thin surface layer. Therefore it could be expected that carbide nanoparticles are emitted in surrounding air by braking.

As mentioned above the process of formation of brake wear debris was model by milling in ball-mill. The results of XRD phase analysis of the milled pad material are given in the table 1. Following significant changes in phase composition during the milling may be observed: (i) the decrease in content of carbon phase (graphite) and (ii) the increase in corundum content. The decrease in graphite phase may due to transition of the graphite structure to the other carbon allotropes, e.g. as shown in [15]. The increase in the corundum content may be due to its separation from other materials in the pad composite.

The second material prepared by the milling was composed of bits of disc and pad in the ratio 1:1. The results of XRD phase analysis of the sample prepared by ball milling of the brake pad and brake disc are given in the table 2. On closer examination may be observed: (i) the decrease in content of carbon phase (graphite) and mullite phase, (ii) the noticeable increase in alpha Fe phase content.

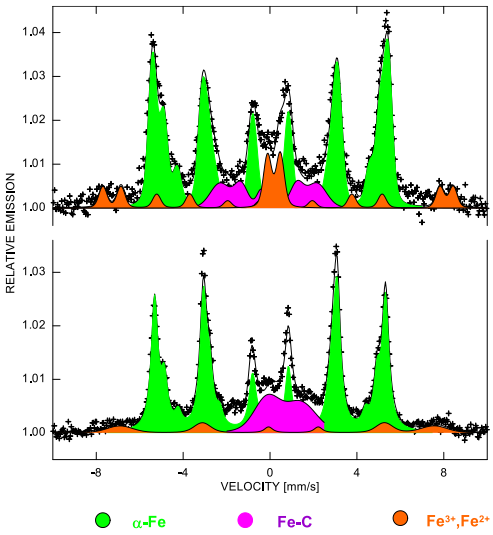


Fig. 4 Mossbauer spectra of the brake disc taken in scattering geometry with detection of 14.4 keV gamma radiation (top) and with detection of conversion electrons (bottom).

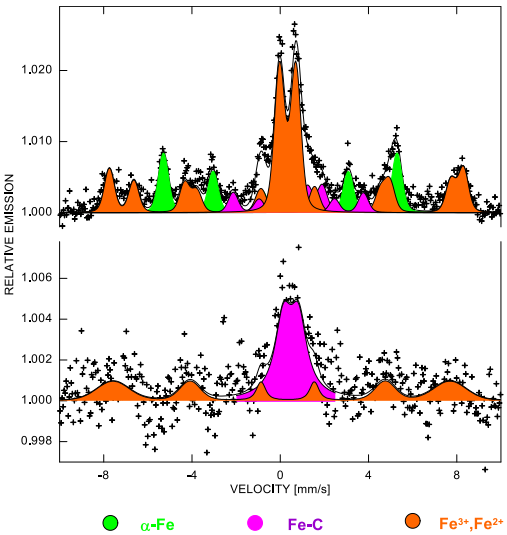


Fig. 5 Mossbauer spectra of the brake pad taken in scattering geometry with detection of 14.4 keV gamma radiation (top) and with detection of conversion electrons (bottom).

In the Mössbauer spectrum of the ball milled powder the sextets of alpha Fe phase of the disk dominate (see fig. 3). As minorite components the sextets of iron carbide and iron oxides can be recognized. Two doublets of paramagnetic phase can be analyzed there and they can be ascribed to iron sulphide and to superparamagnetic iron oxide phases.

Table 1 The amount of dominate crystalline phases determined by XRD (wt %) – milled brake pad.

	α -Fe ferrite	**FeS_2** pyrite	**C** graphite	**$BaSO_4$** barite	**Al_2O_3** corundum	**$CaCO_3$** calcite	**$Al_6Si_2O_{13}$** mullite
Brake pad (BD) - grit *	4	3	69	2	5	7	5
BD- 1 hour milling	4	4	63	3	4	7	9
BD- 2 hour milling	7	7	48	4	6	10	7
BD- 3 hour milling	8	8	47	4	7	9	8

* results for composition of brake pad (original and after ball-milling).

Table 2 The amount of dominate crystalline phases determined by XRD (wt %) – milled brake pad and disc in the ratio 1:1.

	α -Fe ferrite	**FeS_2** pyrite	**C** graphite	**$BaSO_4$** barite	**Al_2O_3** corundum	**$CaCO_3$** calcite	**$Al_6Si_2O_{13}$** mullite
BD + BK - 2 h milling	36	5	34	2	4	6	8
BD + BK - 4 h milling	40	5	33	2	5	7	4
BD + BK - 6 h milling	46	5	27	2	5	6	5
BD + BK - 8 h milling	53	5	21	2	5	6	4
BD + BK - 20 h milling	59	5	17	2	7	4	3

4. CONCLUSION

The above analysis of the thin surfaces of the brake discs and brake pads clearly indicate that fine particles and/or nanoparticles based are emitted in the air by car traffic. The phase composition of these particles is based on chemical and phase composition of brake discs and pads but also new phases appear, e.g. carbon based phases and amorphous phases which are formed by severe plastic deformation of the surface layers during braking.

ABBREVIATION

PM10 - Particles which pass through a size-selective inlet with a 50% efficiency cut-off at 10 μm aerodynamic diameter

ACKNOWLEDGEMENTS

The authors acknowledge the support by Central European Institute of Technology (CEITEC) with research infrastructure supported by project CZ.1.05/1.1.00/02.0068 financed from the EU Structural Funds. Part of the work was carried out with the support of core facilities of CEITEC – Central European Institute of Technology under CEITEC – open access project, ID number LM2011020, funded by the Ministry of Education, Youth and Sports of the Czech Republic under the activity „Projects of major infrastructures for research, development and innovations".

REFERENCES

[1] SANDERSON P., DELGADO-SABORIT J.M., HARRISON R.M. A review of chemical and physical characterisation of atmospheric metallic nanoparticles. Atmospheric Environment, Vol.94, 2014, pp. 353-365.

[2] GASSER M., RIEDIKER M., MUELLER L., et al. Toxic effects of brake wear particles on epithelial lung cells in vitro. Particle and Fibre Toxicology. Vol. 6, 2009.

[3] THORPE A., HARRISON R.M. Sources and properties of non-exhaust particulate matter from road traffic: A review. Science of the Total Environment, Vol. 400, No. 1-3, 2008, pp. 270-282.

[4] GRIGORATOS T., MARTINI G. Brake wear particle emissions: a review. Environ Sci Pollut Res, Vol22, No.4, 2015, pp. 2491–2504.

[5] GRIGORATOS T., MARTINI G. Non-exhaust traffic related emissions. Brake and tyre wear PM. Publications Office of the European Union, Luxembourg, 2014.

[6] LAWRENCE S., SOKHI R., et al. Source apportionment of traffic emissions of particulate matter using tunnel measurements. Atmospheric Environment, Vol. 77, 2013, pp. 548-557.

[7] CHAN D., STACHOWIAK G.W. Review of automotive brake friction materials. Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering, Vol. 218, No. 9, 2004, pp. 953-966.

[8] KUKUTSCHOVA J., ROUBÍČEK V. et al. Wear mechanism in automotive brake materials, wear debris and its potential environmental impact. Wear, Vol. 267, No. 5-8, 2009, pp. 807–817.

[9] SANDERS P.G., XU N., DALKA T.M., MARICQ M.M. Size Distributions, Composition, and a Comparison of Dynamometer and Vehicle Tests. Environ. Sci. Technol., Vol. 37, No. 18, 2003, pp. 4060-4069.

[10] KUKUTSCHOVA J., ROUBÍČEK V. et al Wear performance and wear debris of semimetallic automotive rake materials. Wear, Vol. 268, No. 1-2, 2010, pp. 86–93.

[11] KLIKA Z., TOMÁŠEK V., SIMHA MARTYNKOVÁ G., et al. Thermal alteration of the friction material. 1. Changes in the chemical and mineral composition. Hutnické listy, Vol. 61, No.1, 2008, pp. 62- 66 (in Czech).

[12] CUEVA G., et al: Wear resistance of cast irons used in brake disc rotors. Wear, Vol. 255, No. 7, 2003, pp.1256–1260.

[13] ŽÁK T., JIRÁSKOVÁ Y.: CONFIT: Mössbauer spectra fitting program. Surface and Interface Analysis, Vol. 38, No. 4, 2006, pp. 710-714.

[14] GURUNATH P.V., BIJWE J. Potential exploration of novel green resins as binders for NAO friction composites in severe operating conditions. Wear, Vol. 267, No. 5–8, 2009, pp. 789–796.

[15] WEN B., ZHAO J., LI T., DONG CH. n-diamond: an intermediate state between rhombohedral graphite and diamond? New Journal of Physics, Vol. 8, No. 5, 2006, pp. 62 -72.