Wear debris materials from brake systems: environmental and health issues

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Abstract

The environmental and health concerns related to Particulate Matter (PM) released in the environment from different sources have attracted increasing attention in recent years. The present paper is focused on the PM pollution coming from the wear of automotive brake systems. Generally, brake pads have a complex composition containing even more than 30 different components, some of them more polluting than others. The extent of such emissions depends on their physical and chemical properties and on the tribological interactions with the counter face disc during the braking stages. The main topic of the ongoing research regards the potential impact of the emitted PM on the human health, depending on the mechanisms of formation and toxicity of the particles. Since specific epidemiological studies indicated a link between airborne PM and adverse health effects experienced by urban populations throughout the world, it is important to reduce emissions of pollutants at source, i.e. in the present context, brake systems. The EU funded REBRAKE project is one of the many international research projects that are tackling the problem of wear debris emissions from brakes. The first results achieved by REBRAKE team are presented and discussed with regard to the updated situation as emerging from a detailed review of the present knowledge on this topic.
Keywords: REBRAKE project, brake wear, particulate matter, environmental impact, health impact, pin-on-disc, wear testing.

1 Introduction

In order to decrease the impact on human health and on environment, it is important to reduce emissions of pollutants at source. Particulate Matter (PM) released in the environment from industry and traffic have attracted increasing

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attention and concern in recent years as proved by many studies and research efforts carried out all over the world [1–4]. Released PM originates from a number of non-exhaust processes, brake and tyres, involving corrosion and mechanical abrasion, mass concentration that is influenced by location, season, time of day and weather conditions; thus the contribution of each source varies considerably in space and time.

The research presented in this paper is part of a project financed by the European Union that involves the University of Trento, KTH Royal Institute of Technology in Sweden and Brembo S.p.A., an Italian company international leader in the production of brake systems. The research group based at the University of Trento is mainly concerned with the chemical and structural characterization of PM, and in the evaluation of their possible health and environmental impacts. Laboratory experiments are also carried out on a pin-on-disc wear testing apparatus, in order to investigate the fundamental aspects of wear phenomena occurring in brake systems, even for an understanding of the released mechanisms and the composition of wear debris. This is mainly achieved through characterization approaches based on microscopy, spectroscopy and crystallographic techniques.

Health and environmental impacts of PM from brakes are regarded as important criteria for the selection and development of better performing materials and for the design of more effective brake systems.

In Europe and US ambient air quality standards have been developed or are under discussion as concerns novel issues. The Environmental Agencies and WHO are reporting exceeded limits of air pollutants and their increasing effects on human health and environment. In Europe, the effects of poor air quality have been felt the most in urban areas, where the majority of the European population lives, leading to adverse effects on public health and on ecosystems, where the pressures of air pollution impairs vegetation growth and harms biodiversity [5–7]. It is estimated that two-thirds of the protected sites in the EU Natura 2000 network are currently under severe threat from air pollution and that every year about two million people die due to the effects of atmospheric pollution [8, 9]. Human health is the most vulnerable sector and many reports are showing a negative impact of air pollution on respiratory or cardiovascular morbidity, cancer, increased hospital admissions and even increased rate of death.

2 Brake wear related pollution

In order to protect human health and the environment EU standards were established [10] for exposure limits to several air pollutants. National laws and regulations are targeted more at reducing the exhaust emissions, both gaseous and particulate matter, from engines of road vehicles, traditionally regarded as what is mainly responsible for air pollution from vehicular traffic [11]. Nevertheless, PM from non-exhaust sources provides a further significant contribution to airborne matter. These particles are usually coming from wear of vehicle components, like brakes, tyres, and also road surface. Indeed, data collected by Air Quality in Europe [5] revealed that an important source of trace metals in the urban environment is brake and tyre wear. It is worth nothing that these contributions will be there even when "cleaner" fuels or electrically driven cars will be hopefully more widely used than today.

Particulate matters generated by brake wear are affecting environment and human health in two ways, associated to their size and air concentration, but even to their chemical composition. It was calculated that in Stockholm, passenger cars, goods vehicles and buses released to the environment each year, around 45 t, 7.6 t, and 3.3 t respectively of brake lining materials [12]. The UK National Atmospheric Emissions Inventory [13] indicates that in 2000 brake wear was responsible for 4,200 t of PM_{10} emissions in the UK.

Today's friction brake materials consist of abrasives, friction modifiers, fillers and reinforcements, and binder materials. According to Brake Pad Partnership Project, copper metal, brass, Cu-oxides and Cu-sulphides have become popular additives and, in particular, copper usage in brakes for new automobiles has increased by 40% in the last few years [14]. The concentration of additives as well as their form, distribution, and particle size greatly affects the tribological performance of brake materials. As the braking materials become more complex and contain more species, so are the wear debris generated during sliding. These particles, when trapped in between disc and pads, may result in the formation of the so-called third body or transfer layer. This layer may than fracture and be released, together with other debris, in the environment with subsequent concern [1].

Braking wear and particles emitted into the atmosphere are correlated with driving behavior or frequency and severity of braking events. The highest concentration of brake wear particles occurs during forced fast deceleration, whilst released particles may be directly from the brake mechanism or from wheels, housing these particles from the previous brake events. During the brakes life time, around 80% of the friction material will worn away, and the total wear amount was calculated by Garg *et al.* [15] as 11–18 mg/vkm for cars (vkm = vehicle-kilometer). Luhana *et al.* [13] determined an average brake wear factor as 8.8 mg/vkm, and concluded that smaller number of severe braking events have a larger impact on the amount of lost material.

Of the total amount of brake wear particles emitted, 31% remain in the vehicle, 49% are emitted as fine particulate and 20% precipitates on the ground and in surface water [1].

The main mechanism for particle production is the generation of shear forces by the relative movement of surfaces, when brakes are employed to decelerate the vehicle. A secondary mechanism involves the evaporation of organic compounds of the pads and disc at the high temperatures developed during contact [16].

The rates of brake wear and particles emission are largely influenced by the chemical composition of brake linings, or brake types, and driving mode. In figure 1 the average composition of debris coming from different brake types are displayed and discussed comparatively by Sanders *et al.* [17]. Elemental analysis of the airborne wear debris revealed highest concentrations of Fe, Cu, Si, Ba, K and Ti. It was concluded that in the semi-metallic friction materials, iron mostly comes from the iron powder and steel wool present in the pads, and 90% of the total wear is from the linings. For the low metallic systems, iron is primarily from the wear of cast iron discs, and contributes 60% of the total PM mass. Copper is a high-temperature lubricant present to some degree in almost all linings. Silicon is present in the discs, and silicon oxide is often present in the lining as an abrasive, possibly as silicate phase. Barium sulphate is a common friction modifier. Potassium titanate fibres are present as strengthens in the non-asbestos organic (NAO) lining [17].

A detailed analysis on brake wear particles released during dynamometer tests on low metallic automotive brakes, was conducted by Kukutschova *et al.* [18] and it was observed that size distribution of airborne wear particles varies in dependence of temperature of the friction surface, and the concentration of nano-sized particles (< 100 nm) gradually increased when the bulk temperature of the disc approached 300°C, a temperature at which decomposition of the polymeric binder may occur quite rapidly. Although the tested friction composite was a multicomponent heterogeneous material, the dominant elements in the finest wear particle fractions were iron and carbon. PIXE analysis revealed the presence of Fe, Cu, Sn, Zn and S in all fractions. Raman micro spectroscopy of wear particles revealed the presence of carbon black and graphitic particles.

TEM-diffraction analysis identified the presence of maghemite (γ-Fe_2O_3), magnetite ($FeO.Fe_2O_3$) and hematite (α-Fe_2O_3) in collected fractions of nanoparticles. All wear debris particle fractions contain nano-sized particles down to 20 nm in diameter, most of the times present as clustered agglomerates.

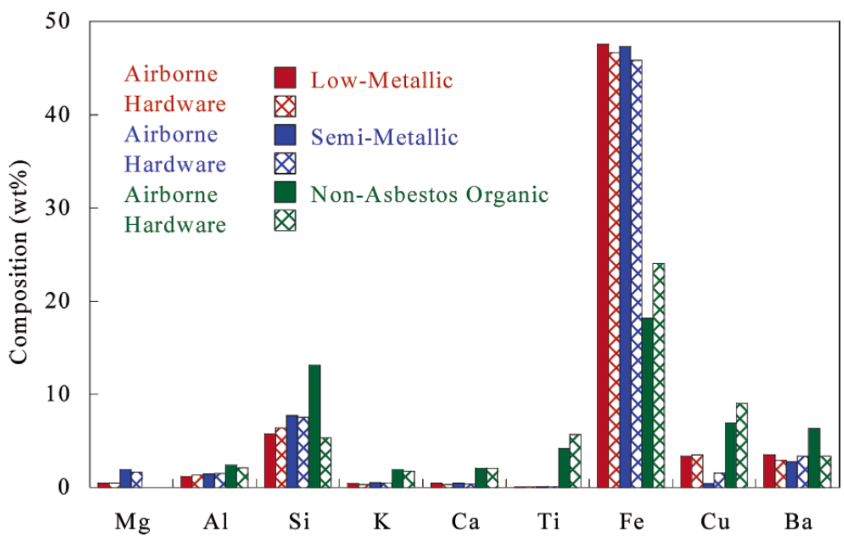

Figure 1: Elemental analysis of the airborne wear debris from low metallic, semi metallic and non-asbestos organic brakes. Both the lining and rotor contributions are presented [17].

Following the statistics data presented by the Netherlands Emission Inventory, the total emission of metals in the atmosphere, generated from brake wear, has decreased considerably in the case of Cu (from 44.6 t in 1985, to 6.26 t in 2006), while the rest of metals, like Ca, Ni, Pb, Sb, Zn, are all reported to be increased [1].

3 Brake wear particles and their effects on human health

Inhaled PM_{10} are deposited in the nose and throat, causing irritations, while fine and ultrafine particles may penetrate deep into the lungs, causing inflammation, create free radicals in the body cells and produce damage to DNA, especially for oxidation reactions and related biological stress.

Several studies proved that the nanosized particles may become blood-borne and be transported to other target tissues and organs, like liver, kidneys, and brain [19]. Nanoparticles enter human body through the skin, lung and gastrointestinal tract [20]. $PM_{2.5}$ penetrates into the small airways and air exchange regions of the lungs. Because of their very small size, nanoparticles can penetrate deeper into the lungs and enter the pulmonary interstitial and vascular space, to be subsequently absorbed directly into the blood stream [21]. Nanoparticles have a large surface area and that makes them more reactive and toxic, thus increasing their detrimental health effects, like pulmonary inflammation and cardiovascular events [20, 22]. They may also move within the body to the central nervous system, the brain, into the systemic circulation and other organs like the already mentioned liver [23].

Metals present in brake wear particles, like iron, copper, manganese, etc., may damage the lung cells tight junctions with a mechanism involving oxidative stress and increase of inflammatory responses [24].

Riediker *et al*. [6] showed that particles that have been confidently traced back to brake wear, resulted to be most likely responsible for health effects like increased heart rhythm, elicits pro-inflammatory and pro-thrombotic. In particular, most of the reported health problems could be associated to metallic component of the brake wear debris.

Study conducted by the US EPA [25] investigated the effects of speed-changing traffic conditions on cardiovascular and haematological phenomena in highway patrol troopers. Effects were seen on heart rate variability, supraventricular atopic beats and the von Willebrand coagulation factor. The strongest correlations were found with fine PM from brake wear and engine emissions, although even a role from crustal material could not be fully excluded [8].

Investigations of toxic effects of brake wear particles on epithelial lung cells *in vitro* conducted by Gasser *et al.* [26] showing that with higher particle concentration, more IL-8 was produced (IL-8 is an important chemokine that is released in the pro-inflammation process by epithelial cells). It has been shown also that carbonaceous nanoparticles induce IL-8 gene transcription in normal human bronchial epithelial cells [27]. It might be assumed that high concentrations of carbon in combination with the small size of the particles nay even increase IL-8 concentrations.

Brake linings have a complex chemical composition which varies a lot in relation with the manufactures, or depending on certain types of brakes. Nevertheless, copper and antimony are considered as fingerprints for brake wear particles. Studies performed in Germany and Netherlands at different locations revealed, an enrichments of these two elements, attributed to brake wear emissions [1, 26, 28]. Netherlands Emission Inventory [1] published a review on road traffic brake wear emissions, based on a number of studies available on brake wear particulate matters. It was concluded that the most important metal pollutants, as concerns scope and toxicity, are Cu, Cd, Ni, Pb, Sb and Zn.

An increased amount of Sb in airborne PM was reported by researchers in Tokyo, US, Germany, Argentina and Northern European Countries. Some of the possible sources of Sb enrichments of airborne particles are automotive brake systems, which contain Sb_2S_3 as a solid lubricant to reduce wear of friction materials. Sb_2S_3 might oxidize to Sb_2O_3, the reaction being kinetically favored by frictional heating during braking, thus becoming a carcinogenic agent [30].

A number of studies are correlating the metal content of brake wear particles to the following health effects: cytokine production, cellular stress, ADN oxidative damage and radical generating capacity. Metals toxicity is due to the high capacity to form reactive oxygen species (ROX) which may cause cell and tissues damaging events [31].

Ghio and Cohen [32] suggest that the inhaled PM interferes with the iron homeostasis in the lung cells and tissues. This disruption results in an oxidative stress which is associated with the initiation and activation of a range of signalling pathways and transcription factor involved in the inflammatory response [31]. Iron may cause conjunctivitis, choroiditis, and retinitis if it contacts and remains in the tissues. Chronic inhalation of excessive concentrations of iron oxide may result in development of a benign pneumoconiosis, called siderosis, which is observable as an x-ray contrast change. Inhalation of excessive concentrations of iron oxide may even enhance the risk of lung cancer [32].

Effects of exposure to antimony are skin and eye effect scan occur from inhaled ions and can result in respiratory effects, e.g. inflammation of the lungs, chronic bronchitis, and chronic emphysema. Specific respiratory effects include antimony pneumoconiosis, alteration in pulmonary function, chronic bronchitis, chronic emphysema, inactive tuberculosis, pleural adhesions and irritation. EPA has not classified antimony for carcinogenicity, as yet [33].

One of the most commonly reported adverse health effect of copper is gastrointestinal distress. Copper is also irritating to the respiratory tract. The liver and kidney are also sensitive targets of toxicity. A number of studies report eye irritation [8], whereas inhalation can result in irritation of nasal mucosa membranes, indirect eye irritation, upper respiratory tract irritation; metallic taste, headache. The liver and kidney are a sensitive target of copper toxicity. In fact, acute copper poisoning can cause liver injury, methemoglobinemia and hemolytic anaemia, dizziness, vomiting and diarrhoea, tachycardia, respiratory difficulty, hemolytic anaemia, liver and kidney failure, and even death [33].

4 The REBRAKE project: an overview

The main task of the international REBRAKE project (see "Introduction") is the development of new materials and systems capable to achieve a 50% reduction in the emission of PM from automotive brakes. One of the leading action of the Project is to achieve a deep understanding of wear mechanisms, that are of course fundamental for an effective and safe braking, although are even the first responsible for the production of debris, contributing to the overall PM concentration in the atmosphere. The study of the wear mechanisms is strongly relying on the characterization of the wear products, in particular wear tracks and debris. The characterization is conducted with a multi-analytical approach using bulk techniques, like X-ray fluorescence (XRF) spectroscopy and X-ray diffractometry (XRD), and single particle analysis (SPA) methods, like scanning electron microscopy (SEM), transmission electron microscopy (TEM) and associated analytical techniques, like energy dispersive X-ray spectroscopy (EDXS). The combination of different experimental tools provides a complete characterization of the starting materials and of the wear debris obtained from laboratory wear tests (e.g. pin-on-disc) or brake bench tests, as concerns their microstructure, chemical composition and crystalline structure. As an example, in figure 2 the surface of a commercial brake pad is shown. The different grey levels in the electron back-scattered image indicate different phases, as indeed proved by EDXS analyses, whose results are displayed in the same figure 2. The dimensional scale of the analyses can be reduced further using a TEM instrument, having ultimate resolution in the subnanometric range, as concerns not only imaging but even spectroscopy and crystallographic information. SPA techniques are even important when a limited amount of debris is available, as in may happen when analysing just the finer fraction of particles collected by active samplers for environmental PM monitoring, that are used not only in on field campaigns but are associated to laboratory wear test equipment, as we made in REBRAKE project.

An important part of the study is to validate the results concerning particles from lab tests with those in atmospheric PM that can be associated to brake wear. A delicate point to tackle is the collection of these fragments that are produce by linear sources, as vehicles, with a diffuse and spatially distributed emission in the environment. In this respect, diffuse (passive) PM sampler are gaining increasing attention and, among them, those using vegetal species, like conifers, mosses and lichens.

In figure 3 a TEM micrograph referring to a TiO_2 based nanometric particle is shown. This can be inferred from the EDXS compositional and crystallographic data (rutile is the majority identified phase), these latter obtained from the selected area electron diffraction (SAED) pattern. The presence of iron and copper can be taken as a reliable indication of the brake provenance of this fragment. The interesting point is that this particle was captured on the surface of moss, contained in a moss bag deliberately placed in the neighbourhood of a tool highway station to monitor PM emission from vehicular traffic [34].

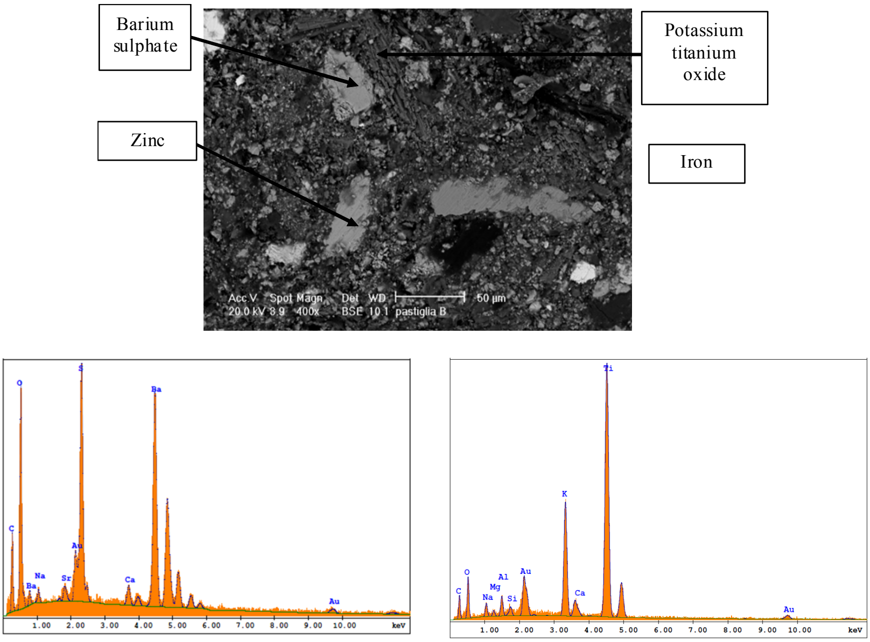

Figure 2: Back-scattered electron image showing the surface of a commercial NAO pad. Some ingredients can be easily identified by SEM observations and EDXS analyses. This is the case of barium sulphate and potassium-titanium oxide whose EDXS spectra are shown (left and right respectively). Gold characteristic X-ray lines are due to the thin coating film deposited onto the sample to prevent electrical charging during SEM observations.

5 Perspectives

The present paper has highlighted the role played by wear debris and fragments coming from automotive brake systems in the PM production and emission in the atmosphere. This concern is a valid and strong justification to the many past and ongoing projects, REBRAKE included, that aim at reducing to a significant extent this source of environmental pollution.

A general approach to the problem, is the production of new materials and brake strategies. In view of the described effects on health and environment, it is advisable that all research efforts would be particular sensitive to these issues. This may definitely help in addressing improvements to critical components only and have a clear hierarchy of the best practices to adopt in all phases of brake lifetime and usage. For this reasons Authors believe that a multidisciplinary approach is paramount to achieve effective and sound results in this field. Moreover, any improvement should be evaluated on the basis of a sufficiently broad number of parameters, going from materials processing, servicing, disposal, environmental and health issues, as described in the previous sections. In this respect, life cycle assessment studies taking into account all relevant parameters and factors are a prerequisite for guiding the research and for rendering the approach more effective in finding truly smart solutions.

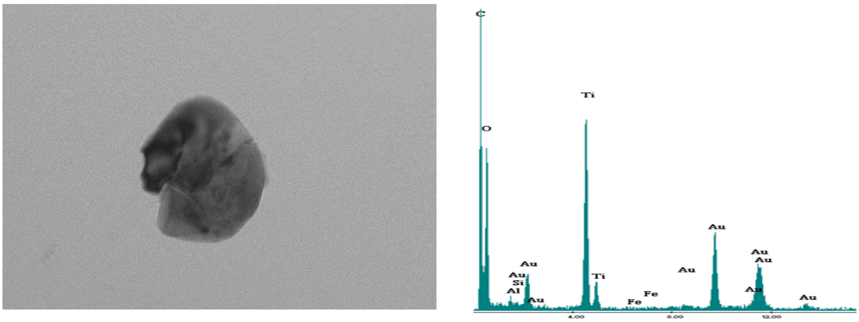

Figure 3: TEM micrograph of a brake wear particle produced by "real" vehicular traffic, monitored using moss bags. The EDXS spectrum (left) and SAED pattern (right) confirm the particle to be made of titanium oxide, rutile phase, with iron and copper impurities. The gold lines visible in the EDXS spectrum belong to the gold carbon coated TEM grid used for preparing the specimen [34].

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