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Abstract: This critical review presents several aspects related to the use of copper as a main component in brake pads in road vehicles. The compositions of these materials are attracting increasing interest and concern due to the relative contribution of wear products to particulate matter emissions in the environment as a result of braking action even though there has been a reduction in exhaust products from internal combustion engines. We review the data on the main wear mechanisms in brake systems and highlight the positive role of copper. However, similar to other heavy metal emissions, even the release of copper into the atmosphere may have important environmental and health effects. Thus, several replacement strategies are being pursued, and the positive and negative features will be critically reviewed. Additionally, the future perspectives in materials development will be discussed.

To the Associate Editor of
Environmental Pollution
Dr. Elena Paoletti

Dear Dr. Paoletti,

We are submitting for the publication in this Journal, as a **review article** the manuscript:
PRESENT KNOWLEDGE AND PERSPECTIVES ON THE ROLE OF COPPER IN BRAKE MATERIALS AND RELATED ENVIRONMENTAL ISSUES: A CRITICAL ASSESSMENT - by G. Straffelini et al.

This is an original paper, which has neither previously, nor simultaneously, in whole or in part been published anywhere else. Moreover we inform you that the text has been professionally edited,
This critical review provides a multisciplinary and holistic view on the functional and environmental role of metallic copper originating from the wear of vehicle brake pads. Wear debris from brake materials are becoming a major environmental issue related to vehicular traffic since, even now that atmospheric pollution from exhaust sources has been drastically reduced, wear of road, tires and, of course, brakes is still providing an important and ever relatively increasing contribution to traffic emissions in the atmosphere. Copper is one component of brake pads and it is attracting a specific interest. Copper fibers and powders are proved to have a very important role in the dynamic of friction layer formation, that is paramount for an effective braking action and brake materials durability. On the other hand copper release is raising a number of health and environmental concerns.
In this review we present several issues, also related to the use and possible replacement for copper in brake linings, thus providing a contribution to the worldwide discussion on this matter.
This study has been carried out in the framework of an European research project on the reduction of car brake emissions, exploiting different experimental and modelling approaches. Some of the original results achieved so far by our reserch team are also included in the manuscript (see Figure 2).
The sensitivity and research expertise developed on the subject together with the wide bibliographic survey provide a solid background to the present paper that we hope may be favorably considered for the publication.

We look forward to your reply!
Yours sincerely.
Stefano Gialanella and co-Athors.

Highlights of the paper:

PRESENT KNOWLEDGE AND PERSPECTIVES ON THE ROLE OF COPPER IN BRAKE MATERIALS AND RELATED ENVIRONMENTAL ISSUES: A CRITICAL ASSESSMENT - by G. Straffelini et al.

- Copper in brake pad materials: role and concerns
- Environmental and health impact of copper
- Copper replacement in frictional brake materials
- International legislation and standards on the above issues

*Manuscript

Present knowledge and perspectives on the role of copper in brake materials and related environmental issues: a critical assessment

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Abstract

This critical review presents several aspects related to the use of copper as a main component in brake pads in road vehicles. The compositions of these materials are attracting increasing interest and concern due to the relative contribution of wear products to particulate matter emissions in the environment as a result of braking action even though there has been a reduction in exhaust products from internal combustion engines. We review the data on the main wear mechanisms in brake systems and highlight the positive role of copper. However, similar to other heavy metal emissions, even the release of copper into the atmosphere may have important environmental and health effects. Thus, several replacement strategies are being pursued, and the positive and negative features will be critically reviewed. Additionally, the future perspectives in materials development will be discussed.

Keywords:
brake pad; particulate matter; wear debris characterization; atmospheric pollution; copper-free brakes

Capsule:
Importance of copper in brake pad materials and concern as regards environmental and health impact of its emission as brake wear product.

Introduction

Friction materials that are used for automotive brake pads are complex mixtures, and they involve several components that are needed to comply with the specific technical and functional requirements to assure safe brake action under different operational conditions (1-3). Recently, environmental requirements for new pad and disc materials are becoming increasingly important due to the increasing contribution of non-exhaust emissions to vehicular traffic pollution (4-5). Copper is one of the most important components in brake pads. In brake linings, copper typically ranges between 1 and 14% in content, and the average concentration of copper in the U.S. and European brake pads is 5% and 10%, respectively (6-9). Copper usage in brake pad formulations has recently become the subject of considerable debate, primarily due to the potentially toxic effects of copper and other heavy metals (10-16) on human health and the environment, such as water quality (17-18). Copper, brass, Cu-oxides and Cu-sulfides have become popular additives, and brake pads are one of the largest sources of copper pollution in urban areas (19). The concentrations of hazardous materials used in brake pad formulations are monitored and controlled by the legislation in the U.S.; however, the overall particulate matter (PM) emissions are the focus of legislation in Europe. A recent study in the San Francisco Bay area, performed within 'The Brake Pad Partnership' (BPP), found that brake pads are major contributors to copper pollution (19). The work by the BPP ultimately led to the adoption of laws in Washington (Senate Bill 6557) and California (Senate Bill 346) that phase copper out of automobile brakes (20-21). Rhode Island, New York and Oregon have introduced similar bills. Figure 1 presents the history of the changing regulations that govern the chemical compounds used in automotive brake pads in the U.S. (22). U.S. legislation currently requires the use of copper to be reduced to <5% by 2021 (low amounts of copper materials) and to be reduced to 0.5% by 2025 (no copper materials). Currently, no specific regulation within the European Union imposes limitations on the use of copper in brake pads.

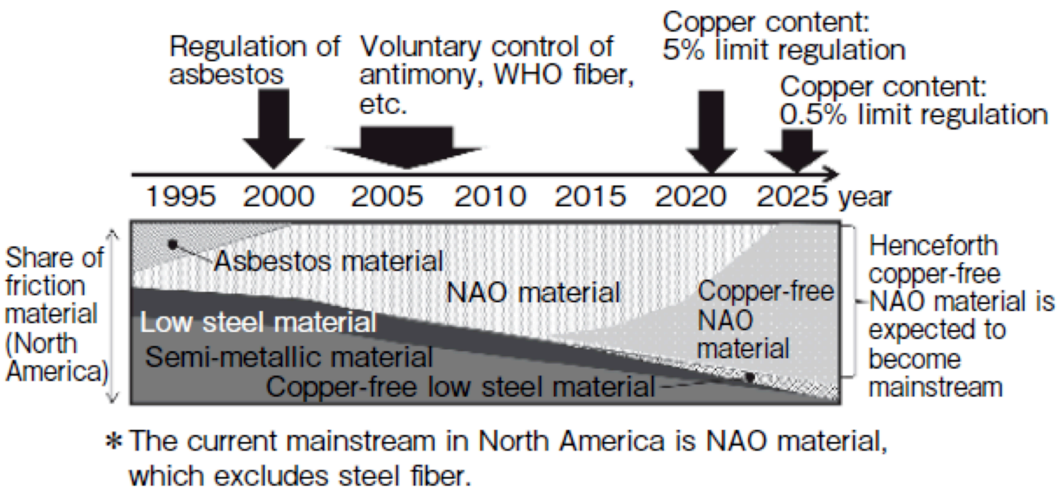

Figure 1. Change in US regulation of chemical substances for brake pads (22).

However, in brake linings, copper is not the only environmental issue relevant to brake materials and their wear. Approximately 50% of the total pad wear has been reported to be emitted as airborne material, which contributes to atmospheric pollution and thus affects human health (*23*). Several studies have been performed to understand the wear mechanisms responsible for the emission of PM (24-31). EU legislation (EU Directive 2008/50/EC and Europe 2020 Thematic Strategy) (32-33) is focusing on PM pollution, especially PM_{10} and $PM_{2.5}$. Such legislation has indicated that brake wear from vehicular traffic is an important source of PM (32-33). In the recent Horizon 2020 "The EU Framework Programme for Research and Innovation" (34), a reduction of PM by 47 wt% by 2020 was highlighted as of the main goals of future European research efforts, in compliance with the EU2020 Thematic Strategy. Simultaneously, new avenues for environmentally friendly impact brakes should be developed to reduce the micro- and nanoparticle emissions and their effects. Legislative measurements for air quality standards have been adopted worldwide (Canadian Council of Ministries of Environment 2003 (35); U.S. EPA 2006 (36); EU Directive 2008/50/EC (32); Australian Government 2012 (37); Government of Japan 2012 (38)) to monitor atmospheric PM, and target limits have been set for both the daily and annual means, particularly for PM_{10} and $PM_{2.5}$. However, to date, there have been no target limits for PM in the nanometric range, such as PM 0.1 and below, i.e., ultra-fine particulate (UFP), even though 80% of the total amount of PM released in the atmosphere from all sources is of this size (39).

The main brake-producing companies are already manufacturing copper-free brake pads in response to U.S. legislation. More than one alternative is used as a copper replacement in brake pad formulations. The goal is to retain the same performance provided by copper or hopefully to improve the performance. New brake pad formulations are being developed under the generic code-names "Cu-free brakes" or "eco-friendly brake pads" (40-50). The elimination of copper and any effort spent to find a suitable replacement should not result in an increase in PM, particularly UFP, emissions in the atmosphere.

Here, we present and discuss some recent advances that are particularly interesting as possible replacements for copper in friction brake pad formulations. First, we present the environmental and toxicological motivations for eliminating copper from friction materials. We also consider the actual role of copper in the wear behavior of friction materials when they slide against a typical cast iron counterface disc. Then, we analyze and discuss the trends in the literature and highlight some topics that require further research considering the environmental issues that are involved.

Environmental and health effects of copper generated from brake wear debris

According to Swedish studies, the estimated annual copper emission as PM was 3,800 kg in 2005. European studies have estimated the copper emission due to brake wear to be 2,400,000 kg (8, 50-56). The particles emitted from brake wear are suspended in the atmosphere and then tend to deposit on the ground, where they can accumulate into creeks, rivers and marine waters (57-62). Vehicle emissions via exhaust and brake pad wear represent the major sources of copper in the runoff from roads (63). The main effects of copper on the aquatic organisms include an imbalance in the aquatic food chain (57) and the rapid death of fish and other aquatic organisms. Copper pollution of river or stream water is one of the reported causes for the extinction of salmon (57,58). Copper-containing storm water runoff from urban landscapes can cause chemosensory deprivation and increased predation mortality in exposed salmon (64). Copper is a neurobehavioral toxicant in fish, and the metal has been known to disrupt the normal function of the fish olfactory system for more than three decades (65-69). The growing debates on the environmental effects of automotive brake pad wear have been supported by a growing number of studies that have shown that metals from brake wear have a direct negative effect on water quality (24,70,71). The presence of metals from brake wear may also be detrimental to aquatic vegetation by promoting the overgrowth of invasive species with a consequent degradation of quality and stability of aquatic communities. (72). *Salvinia Molesta Mitchell* and other aquatic invasive species facilitate the dissolution of metals and micronutrients from brake wear and utilize them to accelerate their growth (72).

Regarding human health, the toxicity of copper has been reported to be relatively low compared with other metals, such as mercury, cadmium, lead, and chromium. Humans are exposed to copper via the inhalation of PM or via copper-contaminated water. Metals in ambient air PM (including copper particles) and, specifically, metals in UFP can generate reactive oxygen species (ROS) in biological tissues (73-75). Oxidative stress may be a major mechanism that causes adverse health effects, and copper is among the more effective metals that induces such oxidative stress.

Evaluation studies on the potential toxicological effects to human epithelial lung cells that have been exposed to freshly generated brake wear particles have shown that particles containing the metals damage tight junctions, and the mechanism involves oxidative stress and increased inflammatory responses. Brake wear particles that contain considerable amounts of iron, copper and organic carbon were correlated with a quantified amount of occludin, a tight junction protein (76-78). Human epithelial lung cells cultured at the air-liquid interface have been used to assess the toxic effects of airborne particle exposure. These lung epithelial cells express tight junctions and produce surfactant when they are exposed to air (79). The occludin concentration decreased significantly with increasing concentrations of brake wear PM metal content. Occludin was also negatively correlated with the intensity of reactive oxidative species (77).

A study of the sources that are potentially responsible for the cardiovascular and hematological effects in highway patrol troopers showed that $PM_{2.5}$, which originates from speed-changing traffic, modulates the autonomic control of the heart rhythm, increases the frequency of premature supraventricular beats and elicits pro-inflammatory and pro-thrombotic responses (76).

Recent studies from Europe have provided results similar to those obtained in the U.S. regarding the potential impact of brake wear debris on both the environment and human health. A European survey on copper pollution is available within the European Union Emission Inventory, but there is no particular reference to brake wear (7,8,24,80,81). Several researchers have estimated the copper concentration over Europe, considering brake wear PM as a major source. Copper concentrations were calculated using the LOTOS-EUROS model using revised emission data from the UNECE-Europe emission inventory (*58*). The results show that brake wear emissions dominate the atmospheric emission in the densely populated countries of Western Europe. Denier van der Gon et al. (7) and Hulskotte et al. (8) have estimated that 75% of the atmospheric copper input in the North Sea may be due to brake wear, and approximately 25% of the total copper input in the Dutch portion of the North Sea may also be from brake wear. Thus, brake wear contributes significantly to the deposition fluxes of copper to surface waters (8, 59, 82-84).

Studies performed in the Czech Republic on semi-metallic brake pads debris have demonstrated the potential impact of brake wear debris (24-25) using particles collected from a dynamometer test and ball-milled semi-metallic brakes. The wear debris composition revealed the presence of copper, iron oxides and carbonaceous components. The mutagenic potential was evaluated in vitro via 2 bacteria micro bioassays, showing the interaction with DNA after metabolic activation. Furthermore, a pulmonary toxicity test on rats revealed an acute response by the lung tissues (24-25). Exposure to PM generated by the brake wear may induce strong inflammatory reactions in bronchial branches. Particles can be retained in the alveolar tissues, cause oxidative stress, and increase the inflammatory responses (24, 76, 79).

Tribological role of copper in friction materials

Automobile friction materials for brake pads contain several ingredients that are subdivided into the following main groups: binders, fillers, friction modifiers and reinforcements (24-26, 42, 85). Copper is a metallic filler that is added in the form of fibers or powders (40). It is generally recognized that copper:

1) improves the thermal conductivity of the pad and thus decreases the contact temperatures (thus decreasing, for example, the so-called thermal fade of brake pads),

2) acts as a reinforcement and forms primary plateaus (possibly after strain hardening) that play a crucial role in the formation of the friction layer, and

3) induces smooth sliding conditions and thus reduces noise generation (41).

Table 1 summarizes the typical elements present in commercial non-asbestos organic (NAO) brake pad materials. The elemental composition values are presented as reference data for the comparative discussion of the composition of wear products.

Table 1. Elemental composition ranges of NAO brake materials (oxygen not quantified)

Elements	Average composition	Elements	Average composition
Zr	0.05-26%	F	3-3.5%
C	20-29%	Zn	3-11%
Ti	0.1-10%	Ba	0-3%
Cu	2-5%	Sn	2-7%
K	0.4-4%	Mg	1-12%
Fe	4-6%	S	1-3%
Ca	4-5%	Bi	0.6-0.8%
Si	3-5%	Hf	0-0.7%
Al	3-8%		

However, recent investigations have proposed additional roles for copper in brake performance. We first review the main results of such recent works and then discuss their possible effects on pollution and health. We also highlight the possible avenues to follow to replace copper in friction pads.

An interesting investigation has been published by Lee et al. (40), who studied the friction and wear performances of a standard NAO pad that contains 8% copper and two modified copper-free samples containing 1.7% hemp fibers and 2.9 or 3.8% of a geopolymer to replace copper. Friction and wear tests were carried out using a full-scale automotive brake dynamometer. The results demonstrated that environmentally friendly pads exhibit a higher wear rate than the reference sample, and they did not develop a suitable friction layer, which was clearly responsible for the lower wear rate. Additionally, the average effectiveness, which is significant for the friction coefficient, was 0.32 for the baseline pad, and it increased to 0.41 and 0.33 for the modified samples containing 1.7% hemp fibers and 2.9 or 3.8% of a geopolymer, respectively. The recorded temperatures at the end of the effectiveness tests were 130°C for the NAO pad with 8% copper and, 140°C and 170°C for the NAO pad with 1.7% hemp fibers and 2.9% or 3.8% of a geopolymer, respectively. Thus, the removal of copper from the pad composition induced an increase in the friction coefficient and a corresponding increase in the contact temperature, although a direct relationship between friction and temperature was not clearly established. These changes were in addition to an increase in the wear rate.

The results raise three main questions that should be addressed in the development of novel brake pad materials:

1) Does copper play a role in the formation of the friction layer? What type of role?

2) What is the role of copper on wear and PM emission?

3) What is the role of the contact temperature and the thermal conductivity of the pad as a result of the copper content?

Lee et al. (40) observed the formation of a compacted friction layer on the worn surface of the reference pad they studied. This layer was not present in the modified copper-free pads. The authors used energy dispersive X-ray spectroscopy (EDXS) analysis to determine the presence of copper in the friction layer, among other components (86). Osterle et al. (26) investigated the characteristics of the friction layer in the case of a conventional NAO material containing 7% copper under severe braking conditions. Using transmission electron microscopy (TEM), they detected the presence of equiaxed copper nanometric grains incorporated into the friction layer. The presence of metallic copper was observed even when the disc surface temperature increased to 650°C during the test. A compacted friction layer formed, and the flake-shaped wear fragments originated from the mechanical damage of the friction layer (in agreement with the observations of Lee et al. (40)). A recent investigation performed by some of the present authors was based on pin-on-disc wear tests and X-ray diffraction (XRD) analysis. The experiments involved a quantitative evaluation of the phases present, and it revealed that approximately 7% of metallic copper was present in the fragments and in the friction layer (87).

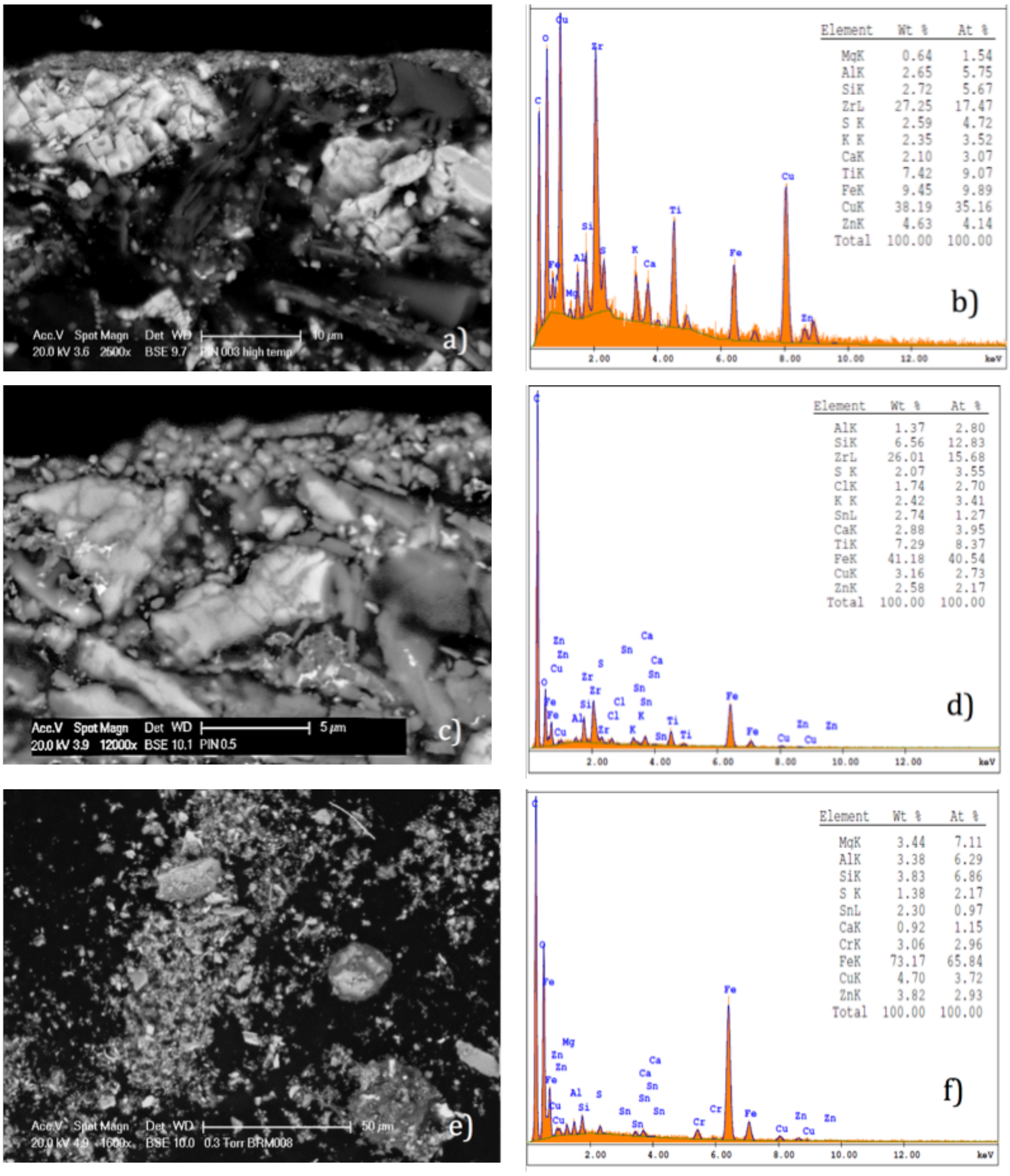

Figure 2. Friction layers formed on the surface of brake pad after pin-on-disc wear tests. (a) well compacted layer and (b) corresponding EDXS spectrum; (c) poorly compacted friction layer and (d) corresponding EDXS spectrum. Brake pad wear debris (e) and corresponding EDXS spectrum (f) from the same wear test and materials as for figures 2 c and 2d. In the EDXS spectra, inset tables with the concentrations obtained from quantification of the EDXS data. Note Cu and Fe concentration values and refer to the main text for relevant comments.

Additionally, the EDXS showed that the most compacted friction layers contained more copper than the less compacted layers. Two examples of brake pad friction layers are displayed in Figure 2. Figure 2a shows the cross section of a well-compacted friction layer. Relevant EDXS data are shown in Figure 2b and confirm the presence of copper with concentrations (approximately 38 wt.% in the present example) fully compatible with the literature values.

Figure 2c displays an example of a less compacted friction layer. From the EDX spectrum in Figure 2d, the presence of considerably less copper (approximately 4 wt.%) was confirmed. A comparable copper concentration (approximately 5 wt.%) was provided by the EDXS analysis (see Figure 2e) performed on the wear debris that was generated by the same brake pad and cast iron disc during the pin-on-disc tests (Figure 2e). Based on the EDXS results (figure 2f), iron was found to be the majority element in the brake wear debris, confirming the central role of cast iron discs in the overall wear of brake systems and the resulting emissions. Copper was confirmed to play an important role in the formation of a well-compacted friction layer that is more adherent to the pad. As proposed by Liu et al. (88), ductile copper spreads and transfers onto the cast iron counterface during sliding. Because of the large plastic deformation that is achieved in the process, progressive strain hardening takes copper to its fracture limit so that fragments may form. These fragments, typically in the sub-micrometer range, become mixed within the transfer layer (88-89). The presence of metallic copper favors the compaction of the transfer layer, which is pressed between the rotating disc and fixed pad (88-89), thus allowing for improved adhesion and compaction within the friction layer.

As noted above, the formation of a compacted friction layer stabilizes the friction coefficient (40), reduces the braking noise (41), and, most importantly, reduces wear (40, 42, 90). Kumar et al. (42, 89, 91) performed braking tests with a dynamometer using different NAO pads with or without metallic fillers, such as copper, brass and iron. They found that an increase in the metallic fillers induced an increase in the friction coefficient because metals were added in the place of barite, which is another brake pad component that is typically added as a fine, smooth powder (42). The addition of copper in particulate form induced a significant decrease in the wear rate, which was attributed to the formation of a more comparatively uniform friction layer.

It is expected that as wear increases the amount of wear debris, the emission of airborne particles would also increase (42). An investigation performed in several European cities showed that the copper in the PM collected along the roads is typically present as a coarse fraction (7, 87, 92-93). This is in agreement with the observation that copper increases the compactness of the friction layer, and the fragmentation of the friction layer results in the formation of wear debris. The finest particles are formed via the disruption of friction layers that contain less copper and are thus more prone to fracturing. Specific investigations should also be performed to assess the role of copper on the particle size distribution of airborne particles that exhibit an influence on human health.

The wear rate of friction materials is strongly influenced by the contact temperature. Particularly, as the contact temperature increases, the wear rate increases and may become quite severe when it reaches the critical value of approximately 300°C for friction materials containing phenolic resins that start decomposing at that temperature (94,95). The average temperature increase, ΔT, in the contact region between the friction material and counterface disc is influenced by different parameters and can be approximated by the following relation (94):

$$\Delta T = \frac{\mu \cdot F \cdot v}{A_n} \cdot \frac{1}{\frac{k_1}{l_1} + \frac{k_2}{l_2}}$$

where μ is the friction coefficient, F is the applied load, v is the sliding speed, A_n is the nominal area of contact, k_1 and k_2 are the thermal conductivities of the contacting materials (the friction material and pearlitic cast iron counterface), and l_1 and l_2 are the relevant thermal distances (93). The thermal conductivity of the friction materials typically ranges between 0.5 and 3 W/mK and is thus considerably lower than that of the cast iron. Additionally, the majority of the friction power is transmitted to the cast iron disc, and it is only approximately 5% of the heat transmitted through the pad (94). Thus, the friction coefficient has a large influence on the contact temperature, whereas the thermal conductivity of the friction material plays only a minor role.

In principle, the copper content in the friction material may influence the contact temperature in two ways: 1) it modifies the thermal conductivity of the pad, and 2) it induces a change in the friction coefficient. For example, Kumar et al. (42) measured the thermal conductivity to be 1.55 W/mK in the pad without copper, and it increased to 2.41 and 2.57 W/mK in the pads with 10% and 20% copper, respectively. For the latter experiments, copper was added to the friction material with a particulate geometry. However, based on the previous discussion, the increasing amount of copper is only a minor contributor to the variation in thermal conductivity and the contact temperature. However, copper plays an indirect role in such variations because it influences the friction coefficient. Lee et al. (40) reported the increase in friction coefficient after the removal of copper from the pad composition (from 8% to 0%), which was attributed to the substantial disappearance of the friction layer. The friction layer may have reduced the number of abrasive interactions that increase friction depending on the angularity of the abrading particles (40). Similar results and conclusions were obtained by Cho et al. (58).

Copper substitution - Current trends and future perspectives

The most important role of copper in friction materials is to facilitate the formation of a compact friction layer, which ensures a number of positive tribological and functional properties to the brake assembly. To replace copper in the brake pad formulation and retain a good brake performance, several modifications and replacements of the actual components are required. Here, some of the proposed alternatives are reviewed and critically analyzed in view of the above-mentioned research results. Consequently, the composition mixture should be reconsidered in copper-free brake pads. A number of studies are underway to find a suitable replacement for copper.

Graphite

Several authors have proposed the replacement of copper with graphite (41, 43), which can be achieved by increasing the typical amount of graphite or other carbonaceous components in the pad materials. Specially designed graphite with improved features has also been considered (43). The influence of graphite on the thermal conductivity of the friction materials should provide an improved dissipation of the frictional heat. Gilardi et al. (41) have shown that an increase in the graphite fraction induces an increase in the thermal conductivity of the pad material, and they also found that such an increase also depends on the graphite grade. In a typical brake-pad formulation, they found that the addition of 8% graphite raised the thermal conductivity from approximately 0.7 to 3.4 W/mK, depending on the graphite product and on the direction of heat flow, i.e., if parallel or perpendicular to the direction of compression of the brake pad. Almost no dependence on the testing temperature was observed when it was kept below the critical decomposition temperatures of the organic components of the brake pad materials. Moreover, the variation in the pad thermal conductivity within the typical ranges did not significantly influence the contact temperature.

Nevertheless, graphite possesses other properties that render it interesting as a component for friction materials. It exhibits excellent mechanical damping properties with beneficial effects on the noise emissions during braking (41,96) and it typically has beneficial lubrication properties. As shown by Osterle et al. (97,98) via simulations, graphite particles enter the friction layer and provide a velocity accommodation between the rotating disc and still pad (97). This produces a stable friction coefficient during braking (97). These analyses ultimately show that graphite and copper should behave nearly identically, justifying the proposed replacement approach.

To date, there have been few experimental investigations on graphite-containing friction materials that are aimed at determining the role of graphite in the formation of the friction layer and on its properties. An interesting investigation on the friction and wear behavior of materials containing synthetic graphite of different particle sizes has been conducted by Kolluri et al. (43, 98). The results showed that the best combination of performance and properties was achieved for the composite containing synthetic graphite with an average particle size of 410 μm. The nature, distribution and extent of secondary frictional plateaus (see Figures 2a and 2c) were correlated with the graphite particle size that was added to the composites. Additionally, the friction coefficients of all composites were reduced by an increase in braking pressure, whereas the reduction was dependent on the graphite particle size. Spherical, non-porous particles of an optimum size not only improve the friction coefficient but also stabilize the pad wear rate (40), as confirmed the proposed model by Osterle et al. (26, 97, 99) regarding the role of graphite in the formation of a homogeneous friction layer.

However, when high concentrations of graphite are used, the material properties, such as the friction features and durability of the pad, are significantly affected because graphite is oxidized to volatile carbon monoxide at elevated temperatures, losing its effectiveness as a solid lubricant (41). Cho et al. (58) determined that graphite that is used as a solid lubricant in brake pad formulations can oxidize above 700°C, and it is released as CO and CO_2, both of which are greenhouse gases. Friction stability, degradation of the braking efficiency and wear of both gray cast iron disks and brake pad materials were affected by the relative amounts of solid lubricants in the friction materials. Improvements in the fade resistance can be obtained by adding Sb_2S_3 because the presence of Sb_2O_3, which forms at the sliding interface, plays a role as a high-temperature solid lubricant (58).

Nanograined copper powder

Nanograined copper powder was investigated by Sharma et al. (100). The aim of using this powder was to reduce the total amount of copper in the friction material while retaining satisfactory friction and wear performances. This could be attained by using nano- and microsized copper powders or by using microcomposite powders with grains containing 10% Cu and an average size of 400-600 μm. In the composite pad material mixture, only a portion (2%) of the micro-powder was replaced by a Cu nanopowder with an average grain size of 50-200 nm. An experimental study was performed on three NAO friction composites to understand the specific effects of copper powder on the functional properties of brake materials. The density, hardness, thermal conductivity and thermal diffusivity increased due to the copper nanopowder inclusions (100). The replacement of the coarse powder with the same amount of nanopowder also resulted in significant improvements in the properties, such as wear resistance, sensitivity of friction to pressure, sliding speed and temperature. The improvement in the tribological performances was ascribed to the surface recrystallization of copper via the formation soft inclusions that are more evenly distributed in the friction layer than coarse particles. Thus, a smooth sliding mode regime was established with a granular layer of mechanically mixed materials. The worn surface topography of the pad and disc were correlated with wear resistance, which was positively influenced by a thin, uniform and coherent film on the counterface of the disc (92,101).

Systematic approach to "eco-friendly" materials

Several studies have been performed in recent years that were devoted to the development of "eco-friendly" or "green" materials in the field of brake assemblies. Several components, including copper, have typically been replaced by other components that were selected so as not to degrade the tribological performances and braking effectiveness.

In the cited investigation by Lee et al. (37, 102), an environmentally friendly geopolymer and natural hemp fibers were used as a fraction replacement of the phenolic resin and synthetic Kevlar fibers in the formulation of Cu-free and Sb-free brakes. The results demonstrated that environmentally friendly brakes exhibit an extensive abrasive wear rate and adhesive mechanisms. Moreover, Cu-free and Sb-free brakes did not develop adequate friction layers, and higher friction values were detected. The poor quality of the brakes was demonstrated by the continuous removal of the friction layers during wear tests. Eventually, more airborne particles were generated that contained a higher amount of the geo-polymer that had a granular morphology and fine wear debris (40).

Lin et al. also investigated the replacement of the phenolic resin matrix of brake pad materials with geo-polymers (45). Geo-polymers are synthetic mineral products that combine the properties of polymers with those of ceramics and cements. To reduce the amount of potentially hazardous particles that are generated by brake wear and to decrease the amount of volatile organic compounds (VOCs) that are released from the brake materials when subjected to temperatures above 300°C, a geopolymer matrix and natural fibers were proposed to replace the phenolic resin and synthetic fibers to strengthen the composite system in which copper was not introduced. The results of this latter investigation were promising, and the novel materials exhibited a good friction coefficient, suggesting that the geo-polymer may be considered as a replacement for copper in low-metallic friction materials (45).

Yun et al. (46) formulated eco-friendly brake friction materials by replacing a portion or all of the metals, the aramid pulp, and the antimony trisulfide with a natural fiber and flaky titanate in a model brake lining formulation. The friction surface and thermal stability of the friction materials were analyzed. Newly developed eco-friendly brake materials exhibited improved wear resistance, which was attributed to the lack of adhesive wear in these materials that contained lower concentrations of metals. The results showed that eco-friendly brake pads exhibit good brake performance, including a relatively stable friction effectiveness, a high fade resistance, a good recovery capacity, and a low sensitivity to speed (45).

New formulations for copper-free brake pads are available and described in several invention patents, such as WO2014024152 A1 (47), that include not only pad materials without copper or copper compounds and alloys but also a complete re-assessment of the design of the fibrous base, featuring a mixture of inorganic (e.g., stainless steel) and/or organic fibers from 1% to 10% in volume that is calculated relative to the total volume of the composite. An eco-friendly proposal for friction materials with a carbon content in the range of 36-51 vol.% was developed in US 20130037360A1 (48). The usage of alkaline-earth metals and carbon fibers was proposed to improve the tribological properties of friction materials containing at least 2-30 wt.% of an alkaline earth-based metallic compound and 2-30 wt.% of carbon fiber, wherein the alkaline earth-based metallic compound is $M_xFe_yTiO_z$ (CN 101948673 A) (49). A formulation for environmentally friendly brake pad materials that contains less heavy metals that showed good resistance to high-temperature thermal degradation, long service life, good wear resistance and a stable friction coefficient can be found in the following reference: WO 2012159286 A1 (50).

Final comments

Here, we have reviewed the research on environmental heavy metal pollution with particular attention to copper content in the atmospheric PM. Road traffic has been recently identified as a major source for metal emissions in urban areas, and brake linings are a primary source of PM emissions. Therefore, the study of the mechanisms involved in the release of metal emissions from brake linings is important to reduce the impact on the environment and human health. However, the replacement of just one component, such as copper, in the brake pad formulation is not typically sufficient to attain significant improvements in both brake performances and PM emissions. Thus, a broader reassessment of the brake pad material is advisable. Subsequently, it is also crucial to monitor the chemical composition, the crystallographic structure and morphology of newly formed species in airborne particles. In new formulations, the use of copper and other potentially hazardous components may be eliminated to comply with international regulations and standards while still retaining suitable friction levels and excellent wear performances. Indeed, the formation of a friction layer, which plays a fundamental role in the tribological behavior of the pad-disc system, is more difficult when copper is removed from the pad materials. This result often leads to an increase in the wear rate with higher friction coefficients and a larger production and emission of airborne wear debris. Even if the environmentally friendly raw materials are used for the bulk formulation, their wear products may still form harmful chemicals (102). Additional research is needed to address the possible impact of these species.

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