Corrosion Stiction in Automotive Braking Systems

The rotor–brake pad assembly for application in automotive braking systems is a complex multimaterial system subjected to several aggressive environments, including rain, snow, and chlorides during winter driving. Corrosion issues involving the rotor–brake pad assembly, in particular for cast-iron rotors, can negatively affect the performance, safety, and reliability of the braking system. Under highly oxidative conditions, electrochemical processes occurring at the gray cast-iron rotor surface can generate corrosion products (iron oxides) that can penetrate the brake pad material through the intrinsic porosity of the friction material employed for the production of the brake pad. The corrosion of gray cast iron discs can lead to a strong adhesion of the brake pad at the pad/disc interface that can impair the reliability and performance of the braking system.

Keywords: braking system; friction material; corrosion; stiction

1. Introduction

The rotor–brake pad assembly for application in automotive braking systems is a complex multimaterial system subjected to several aggressive environments, including rain, snow, and chlorides during winter driving. As a result, corrosion issues involving the rotor–brake pad assembly, in particular for cast-iron rotors, can negatively affect the performance, safety, and reliability of the braking system. Under highly oxidative conditions, electrochemical processes occurring at the gray cast-iron rotor surface can generate corrosion products (iron oxides) that can penetrate the brake pad material through the intrinsic porosity of the friction material employed for the production of the brake pad. Under static conditions, for instance, when the braking pad is activated, this can lead to stiction which consists of a strong adhesion of the pad material on the rotor. This phenomenon can lead to damage to the brake-pad material after releasing the parking brake. In some cases, stiction phenomena can severely affect the performance of the braking system leading, in the worst cases, to the impossibility of driving the vehicle. Another corrosion-related issue in automotive braking systems is the stick-slip phenomenon that can generate noise and vibrations in the braking system.

The automotive industry is strongly oriented towards the replacement of combustion-engine vehicles with electric vehicles. In electric (BEV), hybrid (HEV), and plug-in hybrid (PHEV) vehicles, braking is demanded by the regenerative braking system which is used to recover kinetic energy during braking. Therefore, the rotor–brake pad assembly is strongly undersized and inherently more susceptible to corrosion-related problems than in conventional combustion-engine vehicles.

2. Brake Pad Constituents

Friction materials employed in automotive braking systems are usually composed of more than 20 components. Several hundred ingredients have been reported in the literature for being commonly used to tailor the friction-material properties.

- Binder: to hold the different components together;
- Structural modifiers: typically in the form of reinforcing fibers to provide mechanical strength;
- Friction modifiers: a combination of lubricants and abrasives to adjust the friction properties of the brake pad;
- Fillers: to facilitate the production of the brake pads and reduce their cost.

The different constituents of a friction material can provide different functions including:

- to maintain a high friction coefficient with the rotor during braking;
• to retain sufficient stability at high temperatures;
• to maintain a stable friction coefficient under different braking conditions.

The coefficient of static friction is defined as the ratio between the tangential force to start the relative motion between two bodies and the normal force keeping them in contact. When the bodies are in relative motion with respect to each other, this ratio is referred to as the coefficient of dynamic friction. The friction coefficient is a function of time (or sliding distance). It typically displays an initial transition regime with linear behavior until a peak is reached. This transition regime is followed by a steady state regime corresponding to the stabilization of the friction coefficient. The peak at the end of the transition regime corresponds to the coefficient of static friction, while the steady-state regime is associated with the coefficient of dynamic friction.

The synergistic effect existing between the different ingredients and their influence on the friction properties is extremely complex. Herbert Frood is credited with the invention of the first brake-lining materials in 1897. In 1908, he also introduced, for the first time, the use of a friction material made by the combination of asbestos, brass wire, and resin. Asbestos was a cheap material, thermally stable up to 500 °C with heat resistance, mechanical strength, and processability. Since asbestos is a carcinogenic compound, its elimination led to a sequence of evolutionary stages in the formulation of friction materials. This was mainly accomplished with the introduction of different types of reinforcing fibers.

### 3. Environmental Impact of Corrosion on Braking Systems

The particulate matter produced by vehicle brake pads during braking is recognized as a potentially critical issue linked to the release into the environment of particles not deriving from combustion processes (nonexhaust particle emissions) in the transport sector. In particular, the release of PM10 due to wear of the friction material of automotive braking systems can contribute up to 21% of PM10 emissions due to traffic in urban areas. Up to 35–55% of this particulate matter remains airborne while the remainder can be deposited on vehicle components or the road surface.

The release of heavy metals, such as Cu and Zn, typically present to control the friction coefficient and other properties of brake pad compounds of both the NAO (nonasbestos organic) or LS (low-steel) type, represents another critical issue from an environmental viewpoint that is associated with the wear of the automotive brake system. In addition, the corrosive phenomena of brake discs generally made of cast iron can lead to the release of ferrous oxides or heavy metals in the composition of the friction material into the environment.

The introduction of BEV, HEV, and PHEV vehicles on the market has led to a marked evolution of the braking system with the introduction of electromechanical systems for energy recovery during braking. These recovery systems are generally used for braking with decelerations below 0.3 g (2.94 m/s²) typical of urban driving. For braking with higher decelerations and emergency braking, traditional hydraulic braking systems are used which base their operation on the use of a friction material (brake pads). It follows that the braking of vehicles in urban areas is entrusted for about 90% to the energy recovery system while only the remaining 10% involves the use of brake pads. This has a marked impact on the characteristics required for the friction materials used in BEV, HEV, and PHEV vehicles:

• reduction of the quantity of particulate matter released by the braking system (friction material);
• greater resistance to degradation due to wear compared to vehicles without a regenerative braking system related to the downsizing of the traditional braking system with less mass of the caliper and brake pad;
• reduction of corrosive phenomena of the brake disc to avoid premature wear of the disc–pad system and the phenomenon of stiction (sticking of the pad to the disc during use of the parking brake in environmental conditions of high humidity due to the corrosion of the brake disc).

### 4. Corrosion-Related Phenomena in Braking Systems

As highlighted in the first part of this research, the braking system of a vehicle is very complex since it combines different components, including the brake disk, commonly composed of gray cast iron, the brake pads containing several specific constituents, and anodized aluminum calipers. This complex system can be exposed during service to extremely variable and potentially aggressive conditions, including rain, snow, Sox, and NOx-rich atmospheres and chloride-containing environments. As a result, the components of the braking systems might undergo corrosion during service. In particular, the brake discs are particularly exposed to corrosion due to the intrinsic low corrosion resistance of the gray
cast iron in aggressive environments [19][20]. As discussed above, corrosion affecting the braking system of BEV, HEV, and PHEV vehicles is a critical aspect not only regarding the braking performance but also the emission of particulate matter. In particular, gray cast-iron corrosion can cause different problems ranging from an impaired aesthetic appearance to critical issues connected to the safety and reliability of the braking system. This section focuses on the main corrosion-related issues affecting the braking system of a vehicle.

4.1. Stick-Slip

The stick-slip in a vehicle is associated with a variation of the friction coefficient in the rusted areas of the brake discs. This can generate noise and result in a brake judder. The stick-slip phenomenon can be strongly affected by the formulation of friction material. Shin et al. [21] demonstrated that the friction film formed on the rotor surface was strongly correlated to the composition of the friction material. This affects the corrosion behavior of the disc and can trigger the formation of oxide layers with different thicknesses. Nonsteel friction materials present larger fluctuations of the friction force compared to low-steel materials during the first brake application. This force fluctuation tends to decrease for successive brake applications. The friction fluctuations were associated with the abrasive action of the corrosion products on the brake-disc surface. These corrosion products tend to remain for a longer period on the surface of the brake disk in the case of nonsteel friction materials due to their lower abrasive effect with respect to that of low-steel friction materials. This leads to a higher susceptibility to stick-slip in the case of nonsteel friction materials [22]. Park et al. [4] investigated the stick-slip behavior of nonsteel friction materials coupled with gray cast-iron discs corroded at different levels. In the case of noncorroded discs, the stick-slip amplitude was relatively small and decreased above a critical velocity for which there was a transition from stick-slip to steady sliding. Discs with corrosion products (hematite oxide particles) resulted in higher critical velocities and torque variations during stick-slip testing. This behavior was attributed to an increase in the static friction coefficient related to the transfer of oxide particles from the disc surface to the friction material. Moreover, the friction material exhibited increased wear rates during stick-slip tests with corroded discs due to a marked delamination of the friction film during high-amplitude stick-slip oscillations. The susceptibility to stick-slip can be further enhanced due to the affinity of hematite ($\alpha$-Fe$_2$O$_3$) towards water [23]. In addition to the affinity between iron-corrosion products and water, the effect of humidity on stick-slip behavior is rather controversial. Djafri et al. [24] showed that the coefficient of friction of a cast-iron rotor sample increased with humidity up to 40% relative humidity, whereas it decreased in the interval between 40% and 90%. The decrease of the friction coefficient and wear rate of the friction material at high humidity values were attributed to the formation of a pulverulent and scarcely adherent third body of corrosion products, which could behave as solid lubricants. Similarly, Blau et al. [25] reported for corroded cast iron an initially-high frictional spike followed by a drop in friction relative to the noncorroded material. The lowered friction coefficient persisted for several drags, but it returned to friction levels similar to those of the noncorroded cast iron. The effect was explained by the formation of abrasive scales, while the decrease of the coefficient of friction was related to abrasion and ‘self-dressing’ of the surfaces by fragments of brittle corrosion products.

4.2. Stiction

Stiction is another corrosion-related phenomenon that can affect the performance of the braking system of a vehicle [26][27][28]. It consists of the adhesion of friction material on the surface of the brake disc generating a strong bond at their interface (Figure 1). It typically occurs when the parking brake of a vehicle is activated with an applied static clamping force between the pad and the brake disc. Corrosion products generated by the corrosion of the gray cast-iron disc at the interface with the pad might penetrate into the friction material strongly increasing the possibility of generating a strong adhesion bond between the brake pad and the gray cast-iron disc [29]. This can lead to severe damage to the friction material and, in the worst cases, can prevent a vehicle from moving. The stiction phenomenon is typically observed after a prolonged period of parking, in particular in winter conditions when the pad can be exposed to chloride-containing environments that can strongly enhance the susceptibility to stiction. When stiction occurs in a vehicle, the tangential force necessary to detach the pad from the brake disc can be high enough to cause severe damage to the friction material when the parking brake is released and compromise the safety and efficiency of the braking system [30].
The stiction mechanism is generally well accepted in the literature \cite{21,22-22}. The corrosion processes at the pad–disc interface lead to the formation of soluble corrosion products of the gray cast iron. The permeation of the Fe ion-containing electrolyte and the successive formation of iron oxides at the pad–disc interface after drying is responsible for the establishment of a strong bond between the pad and the rotor (stiction). The susceptibility to stiction is often evaluated by measuring the shear force necessary to detach the pad from the disc \cite{12,13,14}. The stiction mechanism is generally well accepted in the literature \cite{21,22-22}.

The study of the stiction phenomenon is very complicated because it is strongly affected by environmental conditions and, in particular, by the heterogeneous composition of the friction material \cite{23}. As highlighted in the initial part of this research, friction materials contain different constituents that might potentially affect the corrosion behavior of gray cast-iron brake discs and their susceptibility to stiction. In addition, it should be considered that the formulations of friction materials are often proprietary and not disclosed by the producers. As a consequence, the investigation of the stiction phenomenon is rather scarce in the literature and a limited number of papers are available in the literature. Most of the time, research papers are focusing on the understanding the adhesion mechanism between the pad and the brake disc. The adhesion phenomena promoted by the corrosion of the gray cast iron in contact with the friction material are strongly dependent on the corrosion behavior at the pad–brake disc interface. This is extremely complex because it involves the formation of a crevice at this interface that can locally strongly modify the corrosion behavior of the gray cast iron. In addition to parameters affecting the contact between the pad and brake disc, applied pressure and surface roughness can also affect the stiction behavior. Furthermore, it is considered very important to highlight the effect of the chemical and physical properties of the friction material on stiction susceptibility.

5. Approaches to Control Corrosion Stiction in Braking Systems

5.1. Control of Chemical-Physical Properties of the Friction Material

The discussion of the role of the chemical-physical properties on the stiction behavior of the friction material highlights that the first obvious approach to control corrosion-related issues in a braking system should consider the formulation of the friction material. The main areas of action can be summarized as follows:

- Porosity of the friction material: although the effect of porosity is rather controversial in the literature, its control through proper selection of the binder and its content is very important \cite{21,22,23}. Moreover, other constituents of the friction material such as vermiculite might affect the porosity of the friction material \cite{24};

- Mechanical properties of the friction material: friction materials with high stiffness and low compressibility are generally regarded as stiction-resistant materials due to their propensity to reduce the contact area at the pad–disc interface \cite{25}. Proper tailoring of the mechanical properties of the friction material can significantly impact the stiction susceptibility and the extent of the damage of the friction material in case of stiction;

- pH control: the incorporation of additives, sometimes referred to as pH boosters, that can lead to an alkalinization at the pad–disc interface, can reduce the susceptibility to stiction of gray cast-iron rotors \cite{26}. The most employed pH booster is calcium hydroxide;

- Control of local galvanic effects: it is well established that metals in the friction material can promote galvanic corrosion of the gray cast iron \cite{27,28}. In particular, the presence of copper can be detrimental \cite{22}. In contrast, zinc can promote the galvanic protection of the rotor and it can be considered a valid alternative to pH boosters.

Since the friction material can significantly be modified during service, the durability of the friction material plays a key role in retaining its chemical-physical properties and controlling its stiction behavior. Thus, the porosity content of the friction material and its mechanical properties should not be modified by high-temperature exposure during braking. In addition, the effect of pH boosters or metals promoting galvanic protection must be retained for long times in aggressive environments avoiding leaching phenomena or fast oxidation.

5.2. Surface Treatments of the Discs and Coatings

Another approach to control stiction phenomena relies on the surface treatment or the application of coatings on gray cast-iron rotors in order to improve their durability. This will also affect corrosion resistance and stiction behavior. This approach has gained increasing attention for the braking systems of electric vehicles, where the gray cast-iron rotors are...
more exposed to corrosion issues \[35\]. This is also driven by the need to reduce particulate emissions from the braking system of a vehicle \[30\].

In general, a reduction of the susceptibility of gray cast iron is beneficial to control corrosion stiction. This can be obtained through the surface treatment of the gray cast-iron rotors. Holly et al. \[31\] investigated the corrosion behavior of nitrocarburized brake rotors. It was shown that the thermochemical diffusion of nitrogen and carbon inside the cast-iron matrix leads to a marked improvement in the resistance to high-temperature oxidation, scaling, and static corrosion \[31\]. A similar effect can be obtained by means of a coating on the brake rotor \[32\]. A review of the main types of coatings for brake discs is beyond the scope of this work. Nevertheless, different types of coatings are reported in the literature, including hard chrome plating, plasma electrolytic oxidation, laser cladding, and thermal spray coatings \[33\]. These techniques enable the deposition of different types of coatings such as oxides (Al_{2}O_{3}, TiO_{2}, Cr_{2}O_{3}, ZrO_{2}, and MoO_{3}), carbides (WC and Cr_{2}C_{3}) and cermets, Ni alloys, and cobalt–chromium alloys (stellite) \[33\]. As an example, Chioibasu et al. \[34\] reported that the corrosion rate of gray cast-iron brake discs coated with Inconel 718 by direct energy deposition was significantly lower than that of the bare discs. A similar effect is reported also for stellite coatings on gray cast-iron brake discs \[33\].

5.3. pH Boosters and Other Additives

Along with a careful selection of the brake-pads constituents, the use of specific additives is a suitable method to reduce the extent of the stiction phenomenon. The susceptibility to corrosion stiction can be effectively reduced by the incorporation of alkali materials \[34\]. Calcium hydroxide is the most-used anticorrosive filler belonging to this category due to its low cost \[34,35\]. In addition, calcium hydroxide displays low solubility, which enables limiting the fast leaching of the additive during service \[34\]. As discussed above, calcium hydroxide is a pH booster that leads to a local alkalinization at the pad–disc interface reducing the corrosion rate of gray cast iron. Nevertheless, the use of calcium hydroxide may also result in premature cross-linking of the polymeric binder during friction-material mixing. Encapsulation of calcium hydroxide is a possible approach to avoid premature cross-liking \[35\]. Precompounding elastomers with calcium hydroxide is an effective method that can be employed to isolate it from the uncured phenolic resin during friction-material molding \[35\]. This will also allow a controlled release of calcium hydroxide to the braking surface, even after exposure to water during service \[35\]. The size of the precompounding particles must be in the order of 0.5 mm to reduce their surface area, limiting the reaction of calcium hydroxide with the binder. Moreover, encapsulation with elastomers inhibits the curing catalytic effect of calcium hydroxide. Atkinson et al. \[34\] proposed the direct use of a reactive metal, such as calcium, lithium, sodium, or potassium, as a friction-material additive to limit corrosion phenomena in braking systems. Exposure to aqueous solutions of reactive metals leads to their reaction with water through a two-stage reaction. Initially, calcium oxide is formed by a reaction with atmospheric oxygen. This will then react with water to form calcium hydroxide only when the pad–disc interface is exposed to a corrosive environment \[35\]. The incorporation of the reactive metals inside the friction material may be carried out by direct addition, by means of intermetallic compounds, and/or capping in resins or oxides \[34\]. The unreacted metals can also affect the friction characteristics of the composite. Lamport \[35\] proposed also the use of metal phosphates in combination with hydroxides encapsulated in hydrophobic elastomers. In particular, it was claimed that the use of water-soluble phosphates in combination with oxides or hydroxides can be an effective way to protect the brake assembly from corrosion. Different phosphate compounds were considered, including sodium hexametaphosphate, tri-sodium phosphate, di-sodium phosphate, di-sodium polyphosphate, tri-sodium polyphosphate, or sodium pyrophosphate acid \[35\]. Phosphates are well known to form protective iron phosphate films on ferrous alloys. Their combined use with a hydroxide such as calcium hydroxide can lead to a synergistic effect due to the alkalinization at the pad–disc interface. It was shown that the corrosion susceptibility of a pad–disc assembly can be reduced by employing a friction material containing a 3% by volume of a water-soluble phosphate combined with a 3% by volume of calcium hydroxide \[35\]. Encapsulation in a hydrophobic elastomer can also contribute to reducing possible leaching effects due to contact with water or other aggressive electrolytes while preserving at the same time the thermal stability and the coefficient of friction in wetted conditions \[35\].

References


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