



Handbook of Friction Materials and their Applications

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Friction materials: Friction for brakes

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Friction is one of the most common phenomena in nature; it is everywhere in our daily lives without our even noticing it, since it is intimately part of almost everything we do that involves movement or change. It is so common that many times we are not aware that, without it, many aspects of our life would be very difficult, if not impossible. The purpose of this short chapter is not to introduce the reader to the principles of friction, but only to provide a different insight into friction, in order to look at friction, friction materials, and brakes as part of a larger context. A frictionless world would be that ideally depicted in the physics created by Galileo and Newton, characterized by a movement without energy losses. However, the simple acts of holding a water glass with our fingers or walking would be impossible without a friction force that balances and opposes the force of gravity or the reaction force, respectively. Friction makes many things both difficult and possible at the same time: for example, car movement, which consumes energy to feed engines to overcome the friction of wheels against the ground, but also needs the wheels' friction against the ground to make movement possible.

Another important aspect to be mentioned is that friction is characterized by systems composed of many fundamental particles (atoms, molecules, crystals, etc.), such as surfaces in sliding contact, gases, and liquids. Systems composed of many particles imply interactions among them, and therefore imply irreversible processes—that is, a net entropy increment in our world. These interactions can be attractive or repulsive, mechanical, and ultimately they generate forces. This kinetic energy dissipation causes heat and produces wear, as well as many other forms of energy. The science that studies friction between surfaces is called *tribology* and was founded as a new discipline in the 1960s. The major concern at that time was to decrease the coefficient of friction between sliding surfaces and consequently reduce wear in machines, especially those dedicated to manufacturing, so that energy consumption and parts replacement could be improved. Another important topic is *tribochemistry*, which is a new scientific branch dealing with chemical reactions activated by the work of friction. Triboreactions exhibit rates much higher than those of thermally activated chemical reactions.

There is only one technical device in which a high coefficient of friction is desired: the brake. Since machine motion exists, the manner to decrease velocity and stop the motion is a fundamental issue. The need for powerful brakes began when vehicle speeds increased and became necessary to control them. Brakes fulfill this role by transforming kinetic energy into other forms of energy, with heat being the most relevant. This, then, also implies the task of dissipating that heat.

The basic concept of any brake is to dissipate kinetic energy, whether in a horse-drawn carriage, a car, a train or an aircraft; this energy is dissipated through friction

due to viscosity, such as in magnetorheological brakes, or friction between sliding surfaces. The following equation of power dissipation can be considered the basic equation for each type of brake, because it introduces the concept that an external force is necessary and that is the origin of the force opposing motion:

$$\frac{\delta W_d}{dt} = w(\bar{X}) F_N v \quad (1.1)$$

where W_d is work dissipated, t is time, $w(\bar{X})$ is a coefficient of proportionality and $\bar{X}$ the set of variables that affect $w(\bar{X})$, v is the speed, F_N is the force component normal to and between the interacting surfaces, which can be either electric, or magnetic, incident pressure, or a combination of several forces. F_N can be formally considered to be an attractive force between the two opposing surfaces. Controlling F_N means to control the power dissipation and therefore the vehicle and machine speed. This equation highlights the importance of instant dissipation since this determines many surface effects, which depend upon the energy shots rather than on the total amount of energy dissipated.

A more general equation than Equation (1.1) is the following, which relates the friction force to the dissipated power:

$$\frac{\delta W_d}{dt} = F_T v \quad (1.2)$$

In the case of dry friction $w(\bar{X})$ is the coefficient of friction μ , which is affected by temperature, speed, and other variables (for an outlook on the friction law, see the book *Tribology* by I.M. Hutchings [1]), so that μ can be expressed in the following way:

$$\mu(\bar{X}) = \left(\frac{\delta W_d}{dt} \right) / F_N v \quad (1.3)$$

This equation expresses the dependence of the coefficient of friction on some of the main variables that may affect it in vehicle brakes.

For example, consider an 80kW car moving at maximum power to be stopped within 10m and 10s, and if we assume that the two front brakes are dissipating 100% of the kinetic energy, and that each brake pad has an apparent area of 200cm², and a normal force of 10bars applied to the friction material, we obtain that the coefficient of friction must be at least 0.4, which is considered a “magic number” in car brakes.

The power dissipated per unit area is another important aspect that we usually do not think about, but the aforementioned pads dissipate 0.1kWcm⁻² at the maximum power of operation. This is a significant power for a small area; a heavy truck brake pad can dissipate 0.2–1.0kWcm⁻². These facts explain the reason for such a great variety of brake sizes, types and brake lining areas, depending upon the particular application, power, speeds, the vehicle momentum of inertia, and other variables.

For example, aircrafts need to dissipate a great quantity of energy in a small space, so that the dissipated power in Equation (1.3) is very large and consequently so is the amount of heat produced that must be disposed of.

The most important types of brakes currently used are the so-called drum and disk brakes. A detailed description of the different types of brakes (band brakes, different types of drum brakes, clutches, etc.) can be found in the book by Orthwein [2].

The drum brake is normally fitted on the rear axle of small cars, trailers, and trucks. The self-energizing shoe is forced into the drum by the movement of the drum itself, and is mounted so that its friction surface pushes forward of its pivot point, while the de-energizing shoe has the opposite behavior. Trailing and self-energizing action is produced by hooking the heel of the primary shoe to the toe of the secondary shoe (see Figure 1.1). When the wheel cylinder forces the top ends of the shoes against the revolving brake drum, it will try to carry the forward shoe around. As the primary shoe attempts to revolve, it will jam the secondary shoe against the single anchor pin. This stops both shoes and produces a binding effect that helps their function. The purpose of this self-energizing and trailing action is to reduce the amount of needed pedal pressure.

Note how the primary shoe in Figure 1.1 attempts to rotate in the direction of the drum. Since the adjusting screw connects it to the toe of the secondary shoe, the heel of the secondary shoe is jammed against the anchor pin. The role of primary and secondary shoes can be inverted depending on the travel direction of the vehicle.

The torque T can be expressed in the following way for each shoe:

$$T = 2\mu p_0 R^2 b \beta \quad (1.4)$$

where p_0 is the pressure on the shoe surface, R is the drum's inner radius, b the width of the brake shoe, and β is half of the angle of the brake lining (see Figure 1.1) [3].

The disk brake is widely used in ground vehicles, especially passenger cars. However, recently the use of this type of brake has been spreading to many other kinds of ground vehicles: from bikes to heavy trucks and high speed trains. In general, disk brakes offer better braking performances in comparison with drum brakes, since the disk is more quickly cooled. In the past, the solution of disk brakes on the front

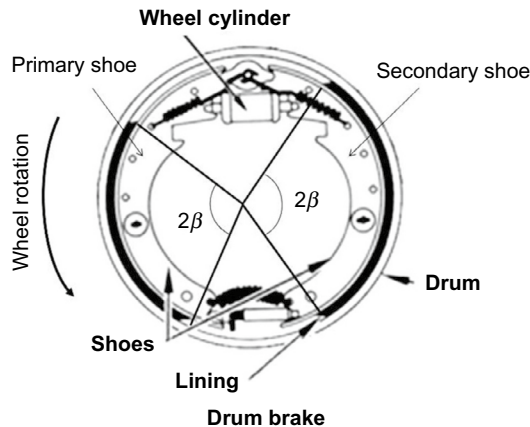


Figure 1.1 Sketch of drum brake.

axle and drums on the rear axle was common. As a consequence disks are less susceptible to the “brake fade” caused when brake components overheat. Most drum brake designs have at least one leading shoe, which gives a servo effect; see primary and secondary shoes (see Figure 1.1). On the contrary, a disk brake has no servo effect and its braking force is proportional to the pressure placed on the brake pad by the braking system via any brake servo, braking pedal or lever. This tends to give the driver a better feeling of control over the braking force.

However, this feeling is affected by the coefficient of friction variations due to conditions such as speed and temperature at which the braking application occurs. Moreover, drums trap worn lining material within the assembly, which may cause braking problems. There are two basic types of disk brakes:

- (i) The sliding disk (floating caliper) brake (Figure 1.2 left) in which the pressure force is supplied by one or more pistons on the side of the caliper. The caliper itself can slide over two pins so that the braking force is also transferred to the brake pads opposite to the piston.
- (ii) The fixed disk (fixed caliper) brake (Figure 1.2 right) in which the pressure force is supplied by one or more pistons on both sides of the caliper.

The braking torque T is calculated according to the following formula:

$$T = \mu N R_m \quad (1.5)$$

where μ is the friction coefficient, N is the clamping force due to the piston (or pistons) and R_m is the average radius of the brake pad to which the friction force F_T is applied. Compared to a drum brake, it requires a higher pressure but is simpler to build (even if more expensive) and has a better and more uniform braking action due to good dissipation of the thermal energy.

The brakes for commercial aircraft, such as Boeing 747 and Airbus, concentrate a lot of energy dissipation in a small space. Their concept is quite different from car brakes.

For a car traveling at 200 km/h, the amount of energy to be absorbed and dissipated is in the order of 1 MJ. For an Airbus A340, it may be over 1 GJ in the extreme case of braking

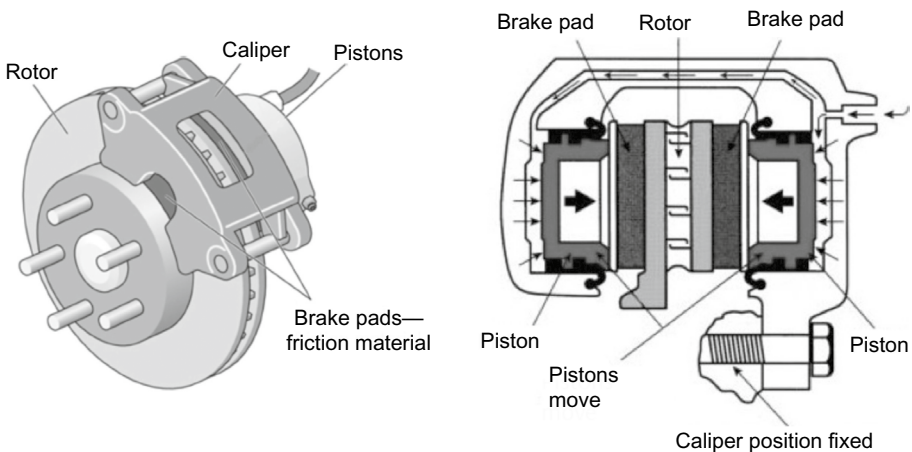


Figure 1.2 Left: sliding disk brake. Right: fixed disk brake.

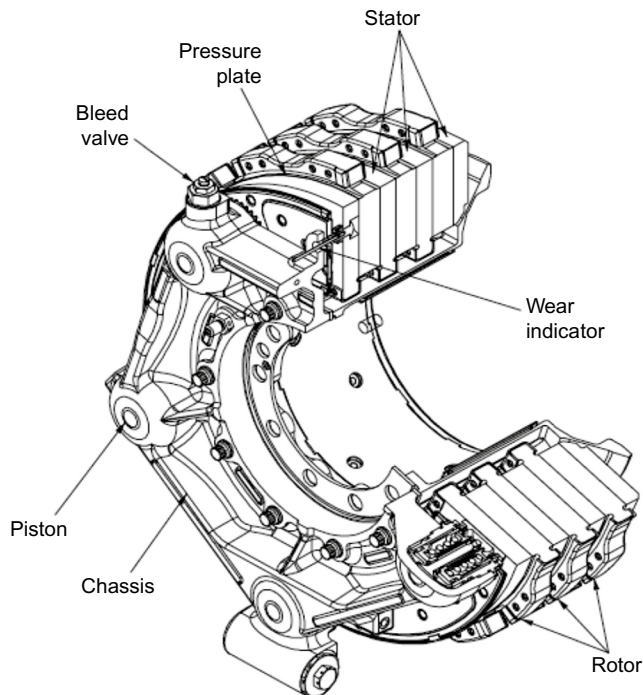


Figure 1.3 Aircraft brake.

J.-J. Sinou, F. Thouverez, L. Jezequel, Comput. Struct. 84 (2006) 1891–1905.

during an aborted takeoff. While two brake pads (per wheel) are sufficient to stop a car, an aircraft needs a stack of disks (rotors and stators) and several pistons, which apply pressure on the stator disk of the friction material in order to increment the power dissipated, adding several terms to Equation (1.2). The stack of rotors and stators is usually called a “heat sink” as an alternative term to brake system. Organic bound material may be sufficient for ground vehicle brakes, but a big aircraft requires a far tougher material offering much higher performance. An image of a section of an aircraft brake is shown in Figure 1.3.

The type of friction to be used in a brake is determined by the application and the brake type. Depending on the shear stress, temperatures and dissipated power, different materials may be necessary. Materials bound by organic binders such as phenolic resins can be stable up to 400 °C, while sintered metals can achieve temperatures in the range of 1000–1500 °C depending on the metallic alloy. Ceramic, carbon–carbon, and carbon–ceramic materials can achieve temperatures above 2000 °C.

References

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Tribology of friction materials

2

2.1 Introduction

The objective of this chapter is to apply the basic concepts of tribology to friction materials in order to define a model to describe and interpret their practical behavior in the tribology of friction materials. The first aspect to be taken into account is that the sliding surfaces are made of different materials. In disk brakes we usually have a composite material, which in most cases is bound by organic resins and faces a rotor, which is usually made of gray cast iron and sometimes of steel or ceramic materials. This simple fact makes the understanding of the tribological phenomena of such materials very complex. Another important point should be underlined: friction occurs in the presence of air, meaning that oxygen and humidity react with elements of the sliding surfaces, altering their physical–chemical and tribological properties. Of course, there are also some effects due to air physically adsorbed onto the materials' surfaces; however, these effects, which are fundamental in the lubrication mechanism of graphite, cannot be compared to the strong effects of oxidation and tribo-oxidation.

In this chapter, brake tests will be not presented or discussed, since the chapter deals with the tribological phenomena and mechanisms that occur in any kind of tests, as well as in real applications. The friction force depends on the materials' properties and topography of the surfaces. Roughness and disk waviness are other issues to be considered in brake sliding contacts. The former determines the types of contacts between the asperities of both surfaces, determining the coefficient of friction, stick-slip, noise, etc., while the latter causes an uneven wear of the rotor, which finally can provoke the so-called *disk thickness variation*, which in turn may cause judder in severe cases.

2.2 Friction force components

The surfaces of friction materials and their counterparts are rough, and the state of this roughness evolves during friction due to several processes involved: plastic deformation, fractures, wear, chemical reactions, and material transfer.

The sum of all the forces resisting the movement at the contact areas constitutes the friction force. Different kinds of grinding result in different surface topography. Heights can have an ordered distribution, such as for a lathe turning with diamond, or disordered, as in shot blasting. The methods used to determine the topography are usually stylus profiling and optical interferometry. An example of a topographical map of a worn rotor is shown in [Figure 2.1 \[1\]](#).

The average roughness R_a is defined in the following way:

$$R_a = \frac{1}{L} \int_0^L |z(s)| ds \quad (2.1)$$

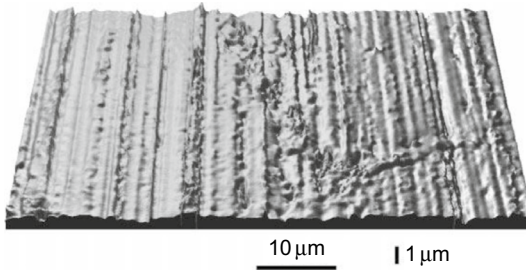


Figure 2.1 Topography of a brake disk surface. Sliding direction of the pad: inwards (optical profilometer).

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where $z(s)$ is the height of the surface above the mean line perpendicular to the motion direction, L is the length of the path, and s is the displacement along the path. Another parameter used is the root mean square deviation of the profile from the mean line R_q :

$$R_a = \frac{1}{L} \int_0^L z(s)^2 ds \quad (2.2)$$

The two quantities are correlated and for a Gaussian distribution $R_q = 1.33R_a$. However, more information is needed in order to have a complete description on the roughness of the surfaces; for example, the distribution of heights (amplitude density function) should be known, for which R_q is the standard deviation. Worn surfaces usually exhibit Gaussian distributions and remarkable differences between the sliding direction and that perpendicular to sliding (see Figure 2.1). The information on how the heights are distributed on the surface may be found in another way. For example, machined surfaces often present some regularities (repetitions).

The power spectral density $P(\omega)$ conveys information on spatial frequencies present in the surface profile, and is the Fourier transform of the autocorrelation function.

The autocorrelation function is given by:

$$C(\delta) = \frac{1}{L} \int_0^L z(s)z(s+\delta)ds \quad (2.3)$$

where δ is a shift distance in the profile path, and when there are regular repetitions the value of $C(\delta)$ varies from low values to higher ones. In the extreme case of a wave function, such as a sinusoid, it is 1 if δ coincides with the wavelength or is null when δ is a half wavelength. Thus, $P(\omega)$, which identifies the periodicities present due to either a particular machining or a surface structure due to friction, is given by:

$$P(\omega) = \frac{2}{\pi} \int_0^\infty C(\delta) \cos \omega \delta d\delta \quad (2.4)$$

Many models of contacts utilize the assumption that contact between two rough surfaces can be described by the contact between a rough surface and a flat one [2–7].

In these cases, the contacts may occur only at the asperity peaks and the contact area is parallel to the mean plane of the surface. However, in the case of the pair pad-rotor, contacts may be oblique and generate force and motion oscillations normal to the mentioned mean surface. There are two terms of the friction force to be considered in a model describing friction between rough surfaces (i.e., almost any surfaces in standard applications): the *adhesion* and the *deformation* terms, both dissipating kinetic energy. This is the basis of the Bowden and Tabor model, which was developed between the 1930s and 1970s [8]. The two terms were treated as completely independent in the simplest version of this model, though later it became clear that they cannot be considered as strictly independent; however, it is convenient to separate their contribution. The adhesion term arises from the attractive forces that act between the asperity junctions, while the deformation term comes from the force necessary to plow the asperity of the harder surface through the softer. In the presented model a certain degree of interaction between the two terms is considered, but only elastic deformations are considered.

In Figure 2.2 the cross section of the contact between two rough sliding surfaces S_1 and S_2 is shown. Two distinct junctions may be distinguished: *assisting contacts*, which possess tangential components in the same direction of motion, and *resisting contacts*, with tangential components in the opposite direction to motion. $Z_1(x)$ and $Z_2(x)$ are the heights to the mean planes of S_1 and S_2 , respectively.

It should be noticed that the model will be discussed in two dimensions (cross sections), *normal* and *tangential*; although projections appear in drawings as straight

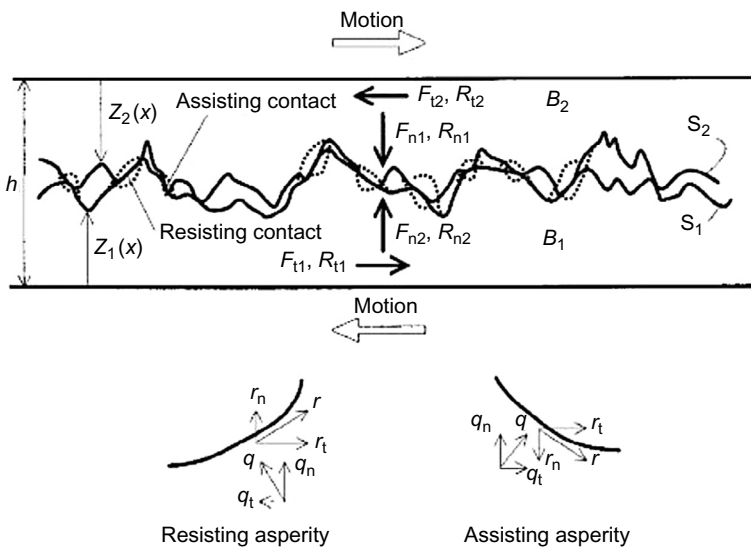


Figure 2.2 Cross section of two rough surfaces S_1 and S_2 in contact. F and R represent sums of the local deformation and adhesion forces, respectively. Subscripts n , t denote normal and tangential components.

M.T. Bengisu, A. Akay, *Stability of friction induced vibrations in multi-degree-of-freedom systems*, *J. Sound Vib.* 171 (1994) 557–570.

lines, we are dealing with contact areas, since the third direction is taken as a constant parameter. For generalized contacts in two dimensions the relationship between the friction force F_T , the normal force F_N , and the two total area projections A_n and A_t (see Figure 2.2) [9] is the following:

$$F_T = F_{dt} + F_{at} = \frac{A_t}{A_n} F_N + \left(1 + \frac{A_t^2}{A_n^2} \right) F_{at} \quad (2.5)$$

where F_{at} and F_{dt} are the tangential (to motion) components of the adhesion force and the deformation force, respectively.

The normal contact force is given by the two normal components of F_N : F_{dn} related to deformation and F_{an} to adhesion:

$$F_N = F_{dn} + F_{an} \quad (2.6)$$

The forces of adhesion and deformation are not completely separated as one might think at first glance. The contact area between the asperities is correlated to deformation, i.e., to the normal load. Greater deformations cause larger contact areas, and consequently larger adhesion components. In the case of metals, fundamental components in organic friction materials, the tangential adhesion force is usually smaller than the normal force F_N , so that the F_{an} contribution to the elastic deformation can be neglected. The elastic deformation by F_{dn} can be treated with the Hertz contact theory with the simplification of spherical asperity tips.

2.2.1 Deformation forces

The energy dissipation during elastic deformation is modeled to the deformation rate of an asperity. This consideration is equivalent to the loss of deformation energy through the propagation of elastic waves into the bulk of the contacting bodies, i.e., radiation loss away from contact areas. Therefore, the sum of the Hertz contact force and a dissipation force that depends on the deformation rate constitutes the elastic deformation force for a single asperity junction:

$$f_{dn} = Ka^{3/2} + \eta \dot{\epsilon} \quad (2.7)$$

where η is the loss factor, a is the contact area between two idealized asperities of spherical shape of radius ρ_1 and ρ_2 , and $\dot{\epsilon}$ is the strain rate.

$$a = \pi \rho \delta \quad (2.8)$$

where ρ is the radius of the composite asperity:

$$\frac{1}{\rho} = \frac{1}{\rho_1} + \frac{1}{\rho_2} \quad (2.9)$$

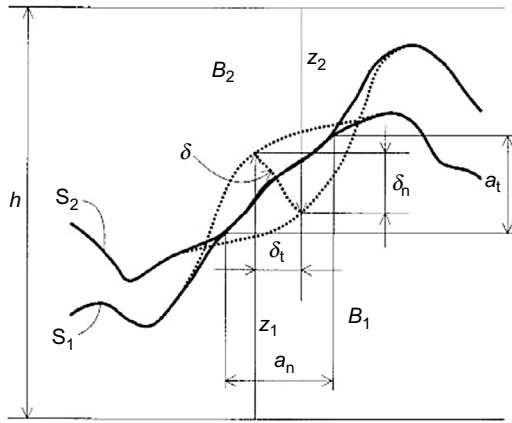


Figure 2.3 Cross section of a typical asperity junction with projections of deformation δ and contact areas a . Solid lines represent deformed surfaces and dotted lines represent undeformed surfaces.

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and δ is the maximum value of deformation, according to the sketch of Figure 2.3, which shows the junction of two asperities as well as the components of deformation on the normal and tangential directions to the mean planes. It is noteworthy to point out that the asperity junctions are supposed to be planar in this model.

The constant K of Equation (2.7) is defined as:

$$K = \frac{4E}{3\rho\pi^{3/2}} \quad (2.10)$$

In Equation (2.10), E is the modulus of elasticity related to the moduli of the two materials of the asperity junction and their Poisson ratios:

$$\frac{1}{E} = \frac{(1-\nu_1^2)}{E_1} + \frac{(1-\nu_2^2)}{E_2} \quad (2.11)$$

Summing the contact areas overall, remembering that the junctions are planar, it is possible to arrive at a formulation of a total normal force F_{dn} :

$$F_{dn} = \sum_i (K_i a_i^{3/2} + \eta_i \dot{\epsilon}_i) \quad (2.12)$$

In principle, this equation cannot be generalized in the case of friction materials at this stage. It would be possible to do this only in the case where all the asperity junctions are composed of the same material couple. This is not obvious, considering that friction materials are composite materials with several and different components, such as metals, sulfides, resins, etc.

2.2.2 Adhesion forces

The adhesion forces taken into account in this model are those caused by a third body which is interposed between the two surfaces. The local adhesion force can be written in the following way:

$$f_a = \tau a + \beta f \quad (2.13)$$

where τ and β are constants and f is the applied load on the junction plane. The sign of both parameters depends on the relative velocity at the interface and is negative for positive relative velocity.

Separation into the normal and tangential components with respect to the mean planes and taking the sum of all the resisting and assisting asperity junctions leads to the following two equations:

$$F_{an} = -\tau A_t - \beta F_{dt} \quad (2.14)$$

$$F_{at} = \tau A_n + \beta F_{dn} \quad (2.15)$$

The signs of Equations (2.14) and (2.15) are a consequence of the convention adopted in Figure 2.2. These two equations are uncoupled for the orthogonality between adhesion and deformation forces. In addition, adhesion forces are not likely to affect those of deformation.

2.2.3 Friction and normal force

The average coefficient of friction is the ratio between the total tangential friction force and the total normal force; substituting the results of Equations (2.14) and (2.15) in Equations (2.5) and (2.6), we obtain:

$$F_T = F_{dt} + F_{at} = F_{dt} + \tau A_n + \beta F_{dn} \quad (2.16)$$

$$F_N = F_{dn} + F_{an} = F_{dn} - \tau A_n - \beta F_{dt} \quad (2.17)$$

Finally, considering Equation (2.5), these equations can be written in the following way, making the time-dependence explicit:

$$F_T(t) = F_{dt}(t) + F_{at}(t) = \frac{A_t(t)}{A_n(t)} F_N(t) + \left[1 + \left(\frac{A_t(t)}{A_n(t)} \right)^2 \right] (\beta F_{dn}(t) + \tau A_n(t)) \quad (2.18)$$

$$p = \frac{F_N(t)}{A_n(t)} \sim \frac{F_{dn}(t)}{A_n(t)} \quad (2.19)$$

The variation of the junction areas and slopes during sliding are factors that greatly affect the evolution of the coefficient of friction μ , which is given by this complex equation:

$$\mu(t) = \frac{F_T(t)}{F_N(t)} = \frac{\beta p + \tau}{p} + \frac{A_t(t)}{A_n(t)} + \frac{\beta p + \tau}{p} \left(\frac{A_t(t)}{A_n(t)} \right)^2 \quad (2.20)$$

In the transient period near the initial stages, the contact areas will be negligible and the coefficient of friction will equal the constant β :

$$\lim_{t \rightarrow 0} \mu(t) = \lim_{t \rightarrow 0} \left(\frac{F_T(t)}{F_N(t)} \right) = \beta \quad (2.21)$$

which is essentially due to the deformation forces, while the adhesion forces effect would begin and increase as bedding advances.

The stick-slip phenomenon is well correlated to noise in brakes (e.g., squeals) and can be described as composed of two phases: the first phase in which the friction force due to resisting asperity contacts must be overcome by the applied tangential force, and the second characterized by consequent assisted slipping when the interface force opposing motion, due to a combination of adhesion and deformation, has been overcome and the accumulated potential energy is released. The exposed model, combined with dynamical equations, shows that stick-slip is correlated to the peaks of the deformation component of the coefficient of friction μ_D at low speed, and also correlated to the surface roughness.

The critical speed v_c depends on the fundamental frequency ν of the friction force, which is related to speed in the following way:

$$v_c \cong \nu \lambda \quad (2.22)$$

The critical speed is the maximum speed at which stick-slip occurs, when the friction force frequency equals one of the resonance frequencies of the system (brake). The wavelength λ represents the average distance between resisting and assisting contacts. The values can be found using Equations (2.3) and (2.4) applied to the slope of the separation between the mean planes of the surfaces. In Figure 2.4, the variation of λ is a function of both the standard deviation of the contact slope and the separation of the mean planes.

At t tending to ∞ the coefficient of friction, defined in Equation (2.20), is determined by the total contact area A_n , which becomes much larger. During the process of friction and repeated braking, as occurs in normal driving as well as in dyno and car tests, the asperities change their conformation, evolving into large and diffused flat contacts made of composite materials, as will be explained in the next sections. This phenomenon is not only due to plastic deformation, but mainly to the deposition of a layer composed of the wear debris.

$$\lim_{t \rightarrow \infty} \mu(t) = \lim_{t \rightarrow \infty} \left(\frac{F_T(t)}{F_N(t)} \right) = \frac{\beta p + \tau}{p} \quad (2.23)$$

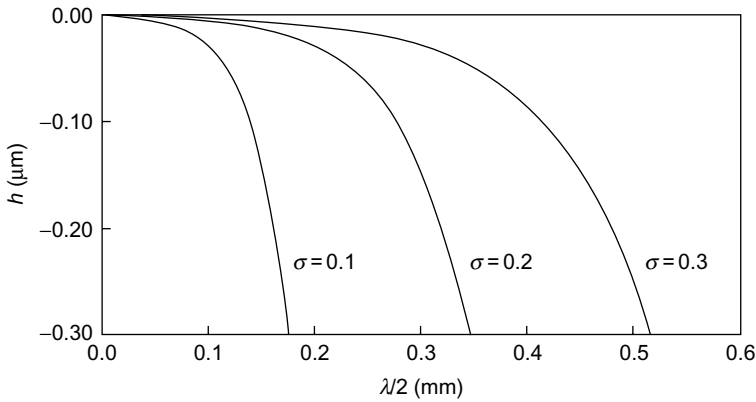


Figure 2.4 Variation of the wavelength λ as a function of the relative separation h and for different values of the standard deviation of contact slope distribution σ .

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where p is the contact pressure and now τ can be easily identified as the shear stress necessary to overcome the asperity junction strength. In the case of fresh surfaces the coefficient of friction will evolve from an initial value determined by the constant β to a term significantly affected by the adhesion forces, as illustrated by the graph of a bedding of a disk brake in Figure 2.5. For a brake system, an initial stage, or systems that are too lubricated, will lead to values of the coefficient of friction close to β , i.e., values probably too low to fulfill their task. This is one of the reasons why balanced

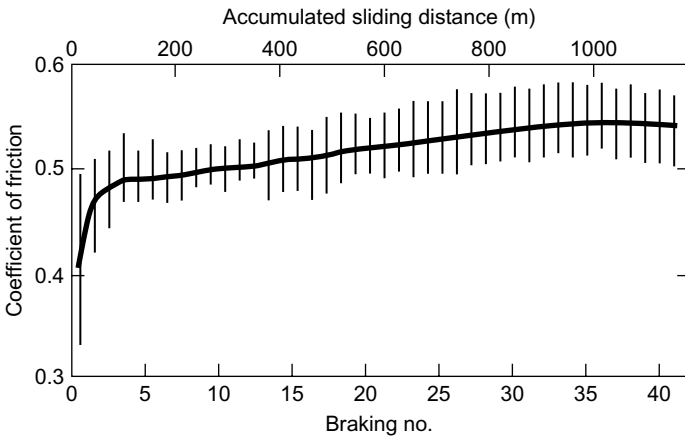


Figure 2.5 In-stop friction increase during a running-in sequence comprising 42 braking applications from 3 to 1 rps at a constant 10 bar brake line pressure. Each stop is represented by a gray line. The black line represents the average coefficient of friction.

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systems of lubricants, abrasives and metals must be used in friction material blends. Nevertheless, this implies a transient stage in which the sliding surfaces are modified and reorganized to achieve a steady coefficient of friction at values suitable for efficient braking applications ($\mu \sim 0.4$) [1].

2.3 Interface structure

The structure of the interface depends on the history of the surfaces. Although surfaces are renewed by wear processes, the temperatures achieved, the power dissipated, the duration of the braking applications, all of these affect the interface. (By the term *interface* we mean the three-body friction.) We can roughly distinguish two situations that characterize the friction brake interface: running-in and steady state. The friction system can be seen as an organized system that requires an energy input to keep the processes working, and it passes from an initial stage to a more steady (evolved) stage, not yet reversible.

Some of the processes have been briefly described in the previous section: elastic deformation, adhesion, asperity junction formation, etc. However, there are other fundamental processes, such as wear due to plowing and wear debris oxidation, which are initial stages. On the other hand, the formation of a composite oxide layer (on both the rotor and the brake pad), and the three-body wear of the layer are all part of cycles that can be considered as steady under certain conditions, and which are summarized in Figure 2.6. It is noteworthy to point out that there is more than one cycle and that, depending upon which cycle is dominating, different friction features can be found, such as severe or mild wear. For example, the upper cycle is mostly characterized by abrasive wear, while the lower one is mostly determined by tribochemical (oxidative) wear. New conditions such as a different pressure or initial speed upset the steady

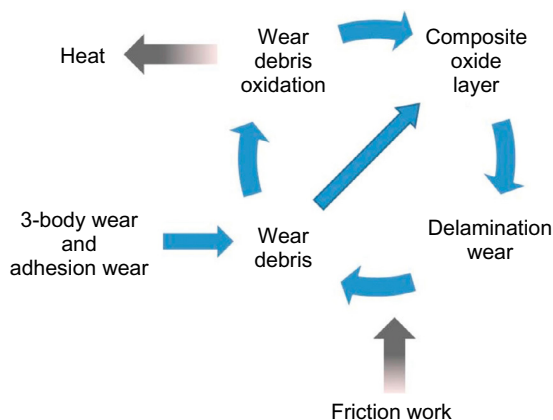


Figure 2.6 Sketch of the friction cycles in steady state conditions, which are activated by an initial stage with dominant abrasive three-body and adhesion wear. The thermodynamic input is friction work, while the output is heat.

state, leading through a transitory state to another new steady state. It should be remembered that the steady state in irreversible processes' thermodynamics plays the same role as equilibrium in thermodynamics. In this perspective, the task of the several ingredients of a friction material formula is to favor the formation of a certain steady state. The steady state is characterized by a minimum of entropy production σ keeping the X_j thermodynamic forces constant with $j \neq i$.

$$\frac{d\sigma}{dX_i} = 0 \quad (2.24)$$

The entropy production is given by several terms, such as those due to the tribochemical reactions, shear strain, wear, etc.

A possible expression for entropy production per unit volume may be the following:

$$\sigma = \sum_i \frac{\xi_i A_i}{T} + \frac{\sum_n \dot{\gamma}_n \tau_n}{T} + \sum_n \frac{\eta_n E \dot{\epsilon}_n}{T} + \frac{Kp}{T} + u(T) \quad (2.25)$$

where ξ_i is the reaction rate of the i th triboreaction occurring on the interface, $\dot{\gamma}_n$ is the shear rate of the n th junction, τ_n is the shear stress necessary to overcome the adhesion force, η_n the loss factor, E is the composed elastic modulus of Equation (2.11), K is the wear rate constant, p the applied pressure, T is absolute temperature, and $u(T)$ includes all the other terms of entropy production.

This equation does not have a practical use in calculating any brake parameters, but is especially useful to underline the complexity of the friction processes of surfaces of composites. It is important to understand that the compounding of friction materials depends on the nature of surfaces, and that there is no univocal effect of a type of ingredient/component. The condition of minimum entropy is, of course, not strictly well respected in brakes over long time periods, as they are systems subjected to many perturbations from the environment. With the exception of some tests far removed from real conditions, this condition can be considered to be respected only in average, passing continuously from an entropy minimum to another very similar value. To give an example, consider the bedding test, in which many brake applications are repeated in similar conditions. If the test series is interrupted for a long time interval, allowing the system to release any type of stress and the temperature to reach equilibrium, when the test data is recovered, the coefficient of friction will have a value lower (around 0.35) than that reached at the previous steady state but much higher than the initial one (see Figure 2.7) [10]. From Figure 2.7, it can be seen that the new steady coefficient of friction, around 0.45, is also reached more quickly, indicating that the transient phase is shortened by the presence of an interface structure already prepared for the friction mechanisms, so that less energy is needed to reach the new steady state, which is completely similar to the previous one since the boundary conditions are the same (application pressure, test temperature, etc.). This coefficient of friction hysteresis indicates that the friction surfaces, although leaving the cycle described in Figure 2.6, can enter into it again easier than at the beginning.

However, under certain approximations, it could be useful to understand and interpret the phenomena occurring on the friction surfaces. The oxide formation is the

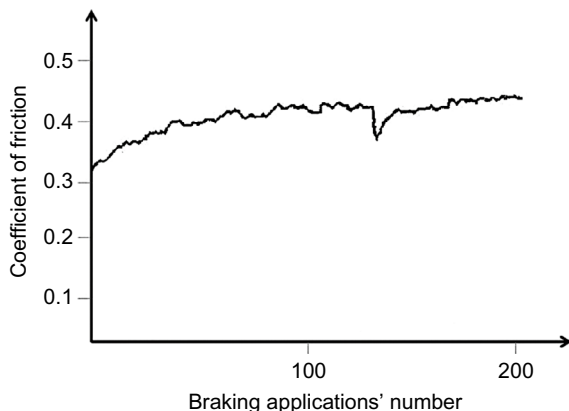


Figure 2.7 Dyno-test bedding for a metallic friction material, interrupted and retaken after 3 h. It is possible to observe the lowering of the coefficient of friction, and the subsequent quick recovery [10].

most important aspect to be considered. The iron oxides found have a composition similar to that of magnetite Fe_3O_4 or, in some cases, wüstite FeO , which often provides a blackish color to the rotor surface. This is due to the amount and penetration of oxygen in air and the surface temperature, which probably stays above 570°C [11]. The tribooxidation of iron in gray cast iron has been studied in detail by Hinrichs et al. [12] with energy-filtered transmission electron microscopy, and other techniques in order to determine the interaction between the graphite flakes of gray cast iron and the tribofilm of magnetite using an organic bound friction material as counterpart. The tribooxidation is fostered by the cracks occurring in the interface between the iron matrix and the graphite flake emerging on the surfaces. These cracks allow oxygen to penetrate and form oxides in a fresh area. Graphite nanoparticles called *nanorods* are detached and become part of the composite layers, which are transformed by the shear friction stresses. The tribofilm is really composed of magnetite and delaminated graphene sheets. Figure 2.8a shows a cross section of a disk surface where a graphite flake is emerging in diagonal and it is possible to observe the magnetite mixing with the graphite nanoparticles.

Therefore, the contact film is a composite material with incorporated graphite nanoparticles as shown in Figure 2.8b. The nanocrystalline nature of the tribofilm was evidenced by TEM analysis which shows interconnected nanocrystals of magnetite and graphene sheets.

Apart from iron oxides, there is a formation of several composite oxides due to metal oxidized coming from the friction material. These oxides form complex layers in both the rotor and friction material surfaces. The rotor worn surfaces are characterized by a composite oxide layer with grooves due to hard particles' plowing and detachments of the layer, which are the dominant contact junctions with the corresponding mating surface. Figure 2.9 shows this characteristic layer on the rotor sliding surface obtained by scanning ion microscopy (SIM) after a run-in test [13]. The oxide

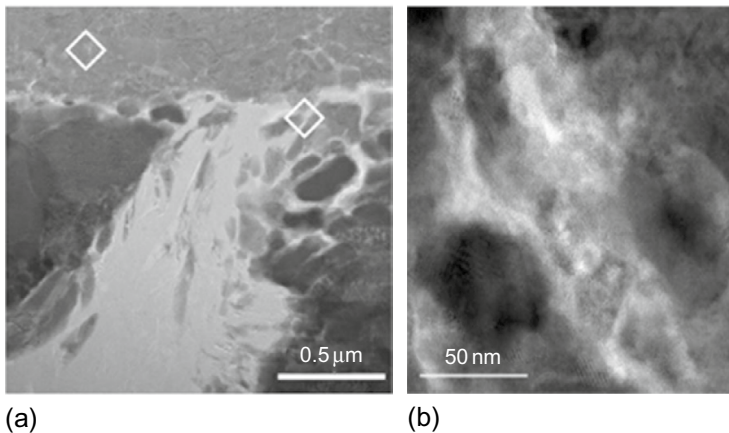


Figure 2.8 (a) Scanning TEM micrograph showing the boundary between the magnetite layer on top, and the cast iron disk with a graphite flake diagonally crossing the iron bulk. (b) Magnification of left square, showing the nanoparticles of graphite incorporated inside the tribofilm.

R. Hinrichs, M.A.Z. Vasconcellos, W. Österle, C. Prietzel, A TEM snapshot of magnetite formation in brakes: the role of the disc's cast iron graphite lamellae in third body formation, Wear 270 (2011) 365.

layer, with a variable thickness from 1–2 μm up to 10 μm, lays on a thicker layer deformed by friction stresses; below this layer it is possible to observe the intact pearlite microstructure of gray cast iron.

The transfer of material from the pad to the rotor especially involves metals that are oxidized and become part of the composite layer. A similar friction film can also be found on the brake pad. However, in this case we can distinguish a tribofilm and a thicker friction layer. Figure 2.10 shows a view of a pad section close to the sliding surface.

Microscopic contact areas of the pad showed bright contrast in SIM. This was attributed to severe plastic deformation finally leading to a nanocrystalline microstructure, in accordance with what was found by Hinrichs et al. on the disk surface. Metallic particles of the pad, the so-called primary contact areas, were mostly covered with a smooth oxide layer, very often less than 1 μm thickness. Above this layer a thin (100 nm), partly amorphous film was often observed. The film was not only restricted to the metal particles, but also spread over adjacent regions, suggesting that secondary plateaus had formed. Similar layers and films, although with slightly different composition and structure, were also observed at the surface of the rotor [13].

It is possible to conclude that, in a steady state, the tribofilm of both the disk and the pad are identically made of a composite oxide layer, mostly composed of nanocrystalline magnetite and graphite nanosheets and other metal oxide particles, depending upon the friction material composition. The new formulas of the last decade have fewer steel fibers and less aggressive abrasives together with metals such as copper, copper alloys such as bronzes and brass tin, antimony and zinc. Nevertheless,

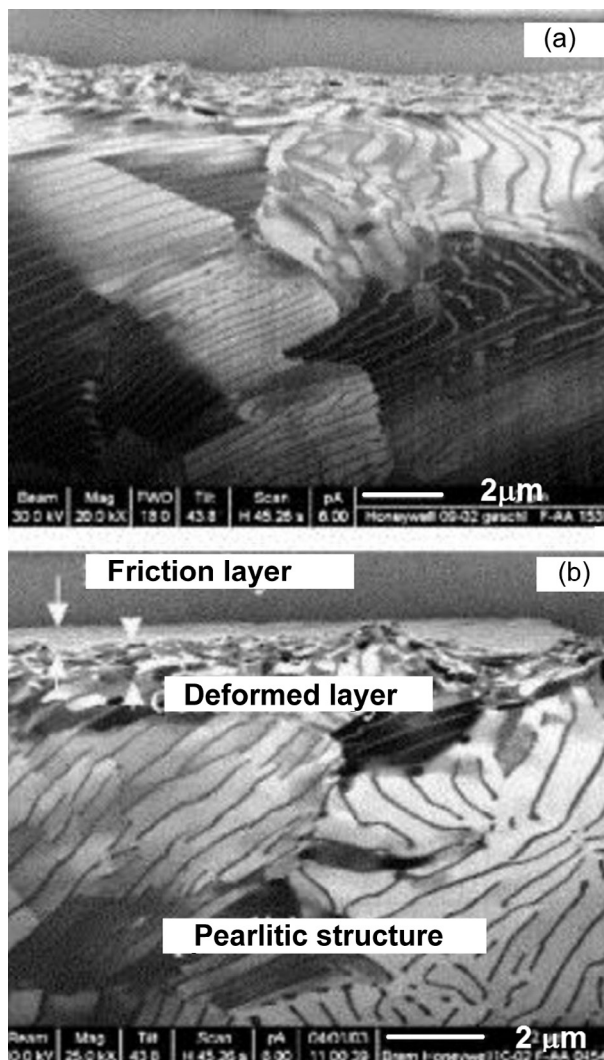


Figure 2.9 Cross-sectional SIM-micrographs of superficial layers of the rotor: (a) machined surface before brake test; (b) rubbed surface after brake test.

W. Österle, I. Urban, *Third body formation on brake pads and rotors*, *Tribol. Int.* 39 (2006) 401.

in the last few years, an inversion of this tendency is occurring, due to the general raw materials' price increases and environmental issues, involving copper in particular. However, the use of strong abrasives such as alumina will not resume. These new materials, often termed *non-asbestos organic*, generate the mentioned composed tribofilm. The utilization of mild abrasives and considerable amounts of solid lubricants, or so-called solid lubricants such as metal sulfides, favor the formation of this composite layer, which includes nanoparticles of graphites, sulfides and metal oxides. Some

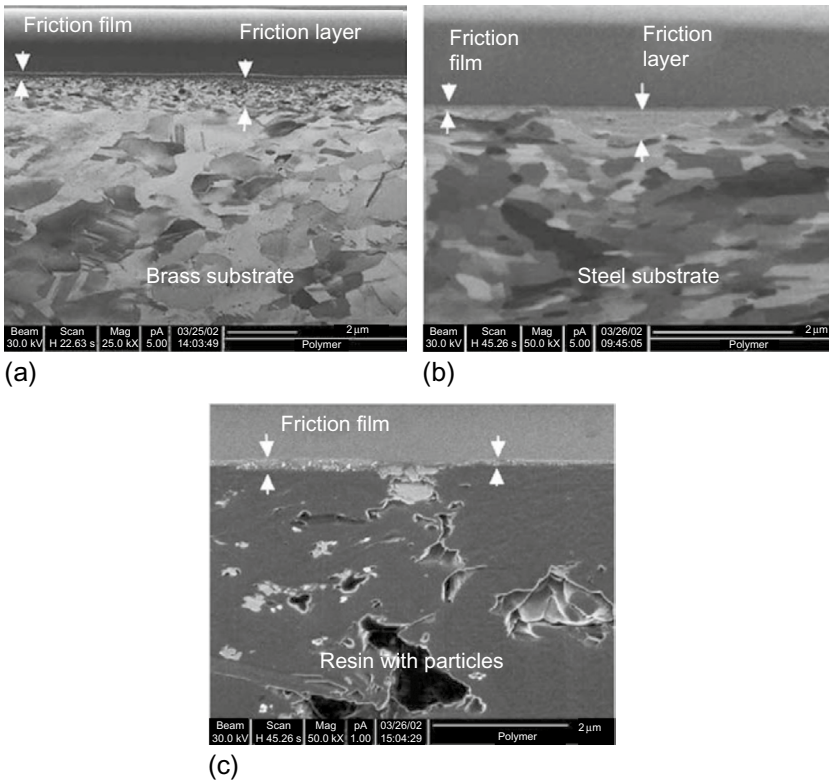


Figure 2.10 Cross-sectional SIM micrographs showing superficial layers on pad constituents: (a) brass particle, (b) steel particle, (c) binder phase.

R. Hinrichs, M.A.Z. Vasconcellos, W. Österle, C. Prietzel, A TEM snapshot of magnetite formation in brakes: the role of the disc's cast iron graphite lamellae in third body formation, *Wear* 270 (2011) 365.

researchers call this layer (or third body) a *mechanically mixed layer* (MML) [14]. This MML will favor the formation of a relatively stable contact area not dominated by high shear force variations, which behaves like a “fluid” leading to smoother tracks of the coefficient of friction. In these cases, several layers can be found on the disk surfaces. The first layer (the most internal layer) contains several components coming from the pad such as fragments of silicates, graphite, sulfides, and metal oxides (depending on the pad composition) in nanocrystalline size. In the second layer, much more magnetite is observed, while the third layer, which is the most external, has a higher content of magnetite and other very fine oxides (see Figure 2.11).

The differences between current ceramic formulas and past formulas can be summarized in the kind of tribofilm found on the rotor surface. Figure 2.12 shows in a sketch these substantial differences. In the first case, in the early stages of non-asbestos materials, the material transfer was from the rotor to the friction material surface and the tribofilm was a composite of magnetite–graphite on both sides; in the

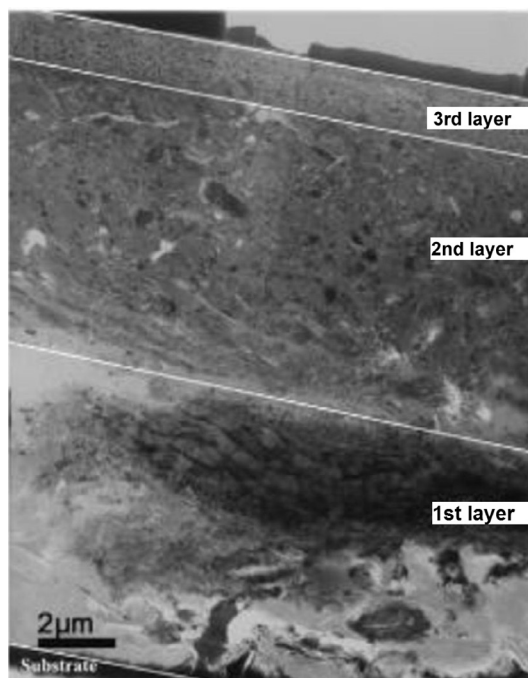


Figure 2.11 TEM image of a thin cross section prepared from the surface film of a cast iron rotor formed during a fading cycle of a dynamometer test procedure.
W. Österle, A.I. Dmitriev, Functionality of conventional brake friction materials – perceptions from findings observed at different length scales, Wear 271 (2011) 2198–2207.

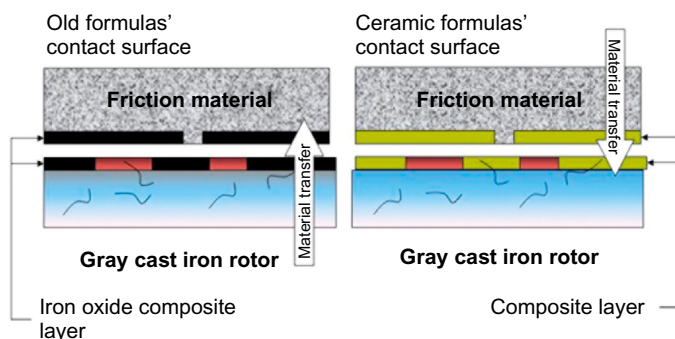


Figure 2.12 The sketch shows the main differences of the tribofilm between old formulas and current ceramic formulas.

second one, there is a significant increment of the transfer from the friction material to the rotor surface, and the layer is more composite.

Other useful equations are those elaborated on by Mueller and Ostermeyer [15], which are the basis for a model of “cellular automaton,” consisting of the dynamics of surface patch growth and destruction. These equations, which are the solutions of

differential dynamic equations for a stationary state, exhibit a dependence on velocity often observed in real brakes—i.e., an increment of the coefficient of friction at low velocities such as occurs at the end of a braking application.

$$\mu = \frac{\eta}{nv(t) + \varepsilon} \quad (2.26)$$

In Equation (2.26), μ is the coefficient of friction, η is a parameter proportional to temperature and power dissipated, the term $nv(t)$ represents velocity, where t is time, and ε is a system parameter. On the other hand, the cellular automaton model describes in detail many characteristics of the brake friction behavior and requires many parameters to be used analytically. Another interesting phenomenon of hysteresis in disk brakes, apparently opposite to that presented in Figure 2.7, is that shown in Figure 2.13, reported by Eriksson et al. [1].

In this case, lowering of the pressure caused an increase of the coefficient of friction. This fact can be interpreted following Equation (2.23), and is explained by the relevance acquired by adhesion forces when a larger contact area is created; this is a phenomenon that cannot be reverted (irreversible processes). In summary, the phenomenon of partial lowering of the coefficient of friction in bedding after an interruption and the increasing of the coefficient of friction after lowering applied pressure can be linked to the same irreversible processes: the irreversible increasing of the contact area.

The curves of Figure 2.13 are based on measurements with increasing pressure followed by decreasing pressure, and vice versa. The pressure was varied at a rate of 1 bar s^{-1} and the sliding speed was held constant at 3 m s^{-1} . The plus signs and circles represent measurement points during increasing and decreasing pressure, respectively. Only a fifth of the points are represented. The solid lines represent the average coefficient of friction [1].

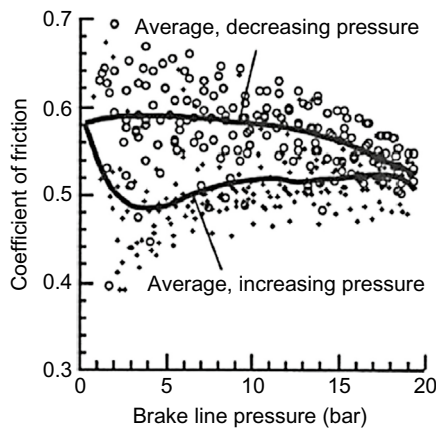


Figure 2.13 Coefficient of friction for an organic brake pad under increasing and decreasing brake pressure.

M. Eriksson, S. Jacobson, *Tribological surfaces of organic brake pads*, *Tribol. Int.* 33 (2000) 817–827.

2.4 Wear of friction materials

The Archard law expresses the wear amount as a function of applied load and displacement, and in general can be used for a wide range of situations. However, the wear constant k of the following equation is a function of temperature and other parameters (for brevity, they are not expressed here):

$$W = k(T) F_N v \quad (2.27)$$

where W is the volume wear rate, F_N is the normal load, and v is velocity. According to the definition of the coefficient of friction provided in Chapter 1 (see Equation 1.3), this equation can be rewritten in the following way:

$$W = KP \quad (2.28)$$

where P is the dissipated power and K is given by:

$$K = \frac{k(T)}{\mu} = \frac{W}{P} = \frac{V}{E} \quad (2.29)$$

Equation (2.29) essentially indicates that the most important parameter is the specific wear rate K which is the ratio between the volume wear rate W and the power dissipated P . In other words, it expresses the worn volume V per unit of energy E .

The tribofilm deposited on the friction material plays a determinant role, and we can say that Equations (2.28) and (2.29), which are referred to as steady state, represent the wear equations of this tribofilm. This tribofilm is worn by several mechanisms, but essentially they are delamination wear, including secondary contacts, i.e., the tribofilms of both surfaces. This kind of wear is characterized by nucleation of subsurface cracks and their propagation parallel to the surface. In general, we can use the term *sliding wear*. This kind of wear is, in any case, determined by the marked oxidative wear of the gray cast iron rotor, which provides most of the debris forming the tribofilm on the material surface (see the delamination forming on the pad surface of Figure 2.14) [16].

The wear debris in this case consist mostly of platelet particles, as shown in Figure 2.15a and b. The wear debris were collected by tests carried out on a full-scale inertial dyno-bench. More platelet particles have been found after long bedding periods (Figure 2.15b). The platelets are formed by submicrometric aggregated grains [17].

The wear debris has a size distribution that can vary with the type of wear mode: (i) an initial stage where abrasive wear prevails or (ii) a steady tribooxidative wear (delamination). The resulting size distribution is often composed of two different size distributions overlapped, such as in the example of Figure 2.16, where the principal distribution is centered around 200 μm and the other around 5 μm . Additionally, most of the larger particles are really agglomerates held together through electrostatic forces [18], but essentially the same type of double distribution is found, where especially large particles are those due to delamination.

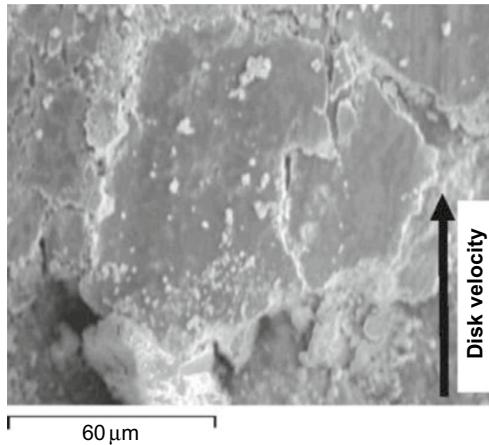


Figure 2.14 Delamination of the tribofilm (contact plateaus) on the brake pad.

F. Massi, Y. Berthier, L. Baillet, Contact surface topography and system dynamics of brake squeal, Wear 265 (2008) 1784–1792.

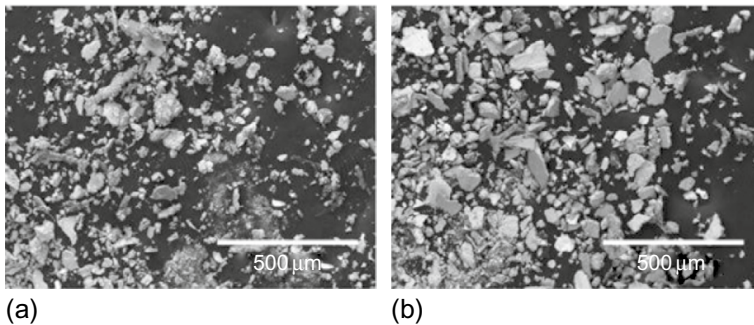


Figure 2.15 Secondary electron images of the debris particles expelled during bedding procedures after (a) 100 cycles and (b) 200 cycles.

R. Hinrichs, M.R.F. Soares, R.G. Lamb, M.R.F. Soares, M.A.Z. Vasconcellos, Phase characterization of debris generated in brake pad coefficient of friction tests, Wear 270 (2011) 515–519.

Transmission Mössbauer analysis and X-ray diffractometry of wear debris from the same series of experiments showed the presence of α -iron (ferrite), magnetite Fe_3O_4 , pyrite FeS_2 , and cementite Fe_3C , and, in minor amounts, wüstite FeO . The composition of the debris may change as a function of the pad. For example, FeS_2 came from chalcopyrite contained in the friction material. Moreover, the series of stop tests carried out at the initial speed of 96 km h^{-1} exhibited more α -iron and cementite than those carried out at 46 km h^{-1} . The change in composition of wear debris, due to the change of composition of both tribofilms (rotor and friction material), led to a more oscillating coefficient of friction as shown in [Figure 2.17](#).

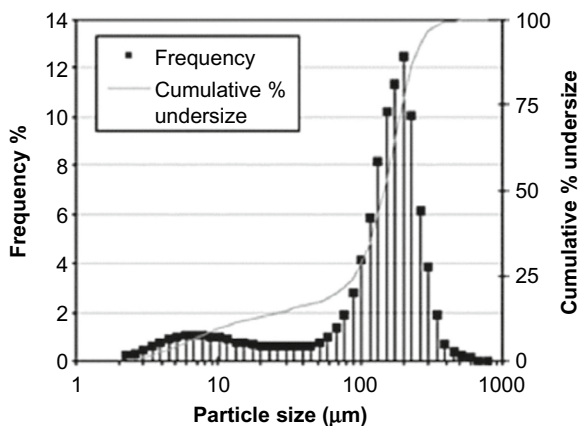


Figure 2.16 Particle size distribution of wear debris from a dyno test of a semimetallic brake pad.

J. Kukutschová, V. Roubíček, K. Malachová, Z. Pavlíčková, R. Holu, V. Micka, D.

MacCrimmon, P. Filip, J. Kubacková, Wear mechanism in automotive brake materials, wear debris and its potential environmental impact, Wear 267 (2009) 807–817.

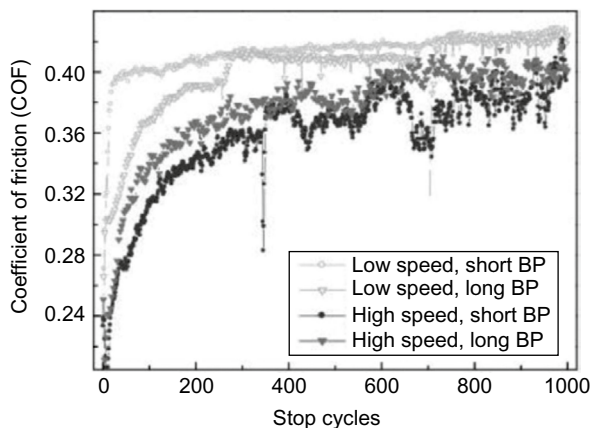


Figure 2.17 Evolution of the coefficient of friction in low and high speed tests as a function of the number of test cycles (after short and long burnishing procedures).

J. Kukutschová, V. Roubíček, K. Malachová, Z. Pavlíčková, R. Holu, V. Micka, D.

MacCrimmon, P. Filip, J. Kubacková, Wear mechanism in automotive brake materials, wear debris and its potential environmental impact, Wear 267 (2009) 807–817.

However, the wear of hard particles, such as three-body wear, cannot be neglected since they are among the main components of friction materials and provide the mechanism of the beginning of the whole wear cycle (see [Figure 2.6](#)). Indeed, the decomposition and wear by oxidation of the organic binder, due to the high local surface temperatures, causes the release of the hard and thermal resistant ceramic particles.

2.4.1 Tribofilm and wear behavior

The creation of a model of friction materials' wear is based on experiments carried out by means of tribometers, which show the relationship between the tribofilm on the friction material and wear rate. Dante et al. carried out a series of tests with different friction materials. M1 was essentially a metallic copper-based material; N1, N2, and N3 were low steel materials with the same formula, but molded at different pressures: 400 bar, 4000 bar, and 600 bar, respectively [19]. The tribofilm is clearly visible and measurable in the SEM image of Figure 2.18 for the N3 material oscillating between 2 and 10 μm .

This series of experiments, executed at a constant torque and different speeds in order to have different dissipated powers (see Table 2.1), shows that the aforementioned specific wear K (Equation 2.29) increased exponentially with increasing the dissipated power. The specific wear K can be considered a constant only at low dissipated powers, as shown by Figure 2.19.

The exponential increasing of the specific wear rate is due to the failure of the tribofilm since the binding considerably decomposes above 400 $^{\circ}\text{C}$. Below the dissipated power of 1 kW cm^{-2} , i.e., in the normal range of automotive applications, the specific wear rate seems to be nearly constant. In this experimental condition, the specific wear rate may be expressed by the following equation:

$$K = \frac{K_0}{\left(1 - \frac{P}{a}\right)} \quad (2.30)$$

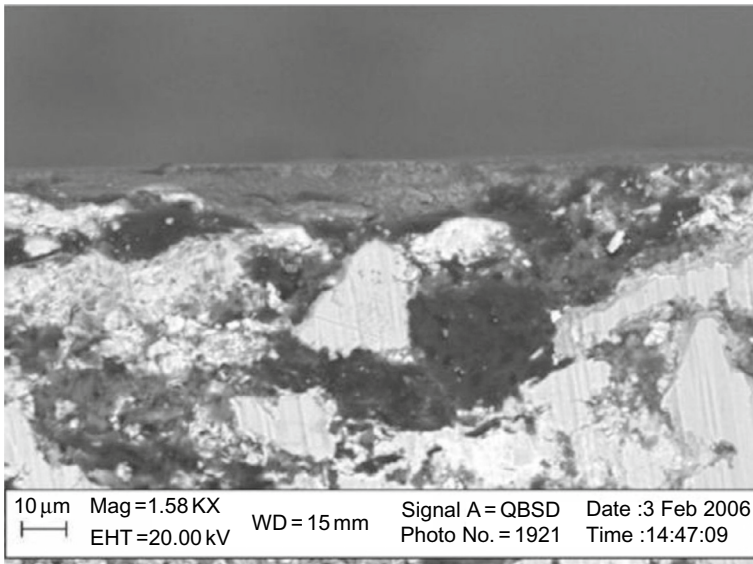


Figure 2.18 Section view of the contact layer of material N3.

R.C. Dante, F. Vannucci, P. Durando, E. Galetto, C.K. Kajdas, *Relationship between wear of friction materials and dissipated power density*, Tribol. Int. 42 (2009) 958–963.

Table 2.1 Experimental conditions of the tribometric tests

Torque (Nm)	Angular speed (rad s ⁻¹)	Power (kJ s ⁻¹)	Power density (kW cm ⁻²)	Final temperature (°C)
35	157	5.5	3.4	450
35	137	4.8	3.0	400
35	114	4.0	2.5	350
35	83.8	2.9	1.8	300
35	52.3	1.8	1.1	250

The temperatures are measured in the middle of the rotor.
R.C. Dante, F. Vannucci, P. Durando, E. Galetto, C.K. Kajdas, Relationship between wear of friction materials and dissipated power density, Tribol. Int. 42 (2009) 958–963.

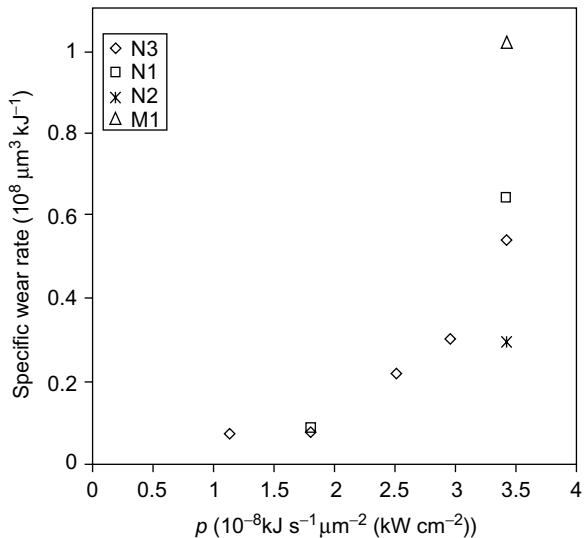


Figure 2.19 The specific wear rate K for materials N1, N2, N3, and M1. The unit of the dissipated power density, expressed as $10^{-8} \text{ kJ s}^{-1} \text{ mm}$, is equivalent to kW cm^{-2} .
R.C. Dante, F. Vannucci, P. Durando, E. Galetto, C.K. Kajdas, Relationship between wear of friction materials and dissipated power density, Tribol. Int. 42 (2009) 958–963.

where K_0 is the specific wear rate at $P \rightarrow 0$, while a is a fitting parameter correlated to shear strength of the tribofilm. An equivalent equation can be obtained with temperature instead of the dissipated power.

It is noteworthy to point out the relevance of K_0 , which is the value extrapolated at null dissipated power. From this value it is possible to determine the energy needed to remove the tribofilm by means of the so-called delamination wear mechanism. The tribofilm average thickness is the smallest thickness that can be removed. Severe wear in friction materials often occurs, especially when the tribofilm removal is more rapid than its growth, and it is too thick.

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Types of friction material formulas

3

3.1 Automotive applications

Automotive brakes, especially disk brakes, are characterized by many denominations following commercial appeal, such as “ceramic materials,” non-asbestos organic (NAO), semimetallic, low metal, hybrid and so on. Sometimes some of the characteristics described are really important, such as the lack of asbestos in formulas of NAO materials. However, in most cases, beyond these different names there is no conceptual difference among the several types of formulas. The progressive elimination of asbestos led to a sequence of evolutionary stages. The first challenge that materials engineers had to face was the search for a fiber that could adequately substitute for asbestos. The characteristics that made asbestos so appreciated and widespread in friction materials were its fibrous nature, low density, thermal insulation, mild wear and stable coefficient of friction. At first it seemed complicated to find a substitute for such a multifunctional material since organic fibers—although good insulators in general and in certain cases exhibiting good mechanical strength, such as in the case of aramid fibers—decompose and do not contribute to the stability coefficient of friction. Moreover, the decomposition of these fibers weakens the material structure, causing a wear increment. On the other hand, metallic fibers such as steel fiber, although contributing to mechanical strength, increase the coefficient of friction, have a high density, and are good thermal conductors. All these facts favored the elaboration of complex formulas with many raw materials to replace asbestos. Copper (as powder and fiber) and steel fibers became two important ingredients for friction materials. Although the role of copper is often related to its high thermal conductivity, its contribution to conductivity near the surface is still unclear. However, the transfer of copper to the composite disk tribofilm is a well-known phenomenon. In the United States, The Brake Pad Partnership [1] reached consensus that the most effective course of action would be to pursue legislation that reduces the amount of copper used in brakes to an insignificant amount in a phased manner. The resulting bill, SB 346, which became law in September 2010, places a 5% by weight limit on the copper amount used in brakes sold in California by 2021, and reduces that percentage to 0.5% by 2032. The brakes developed to meet these requirements must also meet all applicable safety and performance standards. Other states will follow the example of California legislation.

Other restraints on copper content will likely be introduced in other states in the United States. In any case, the general trend after asbestos banning is to decrease and eliminate all the hazardous and toxic elements or compounds in friction formulas.

The evolution of friction formulas is outlined in [Figure 3.1](#), where the main challenges faced in the last two decades are presented with their solutions. This led to materials with many metals and metal sulfides. The current trend is to reduce the content of heavy metals.

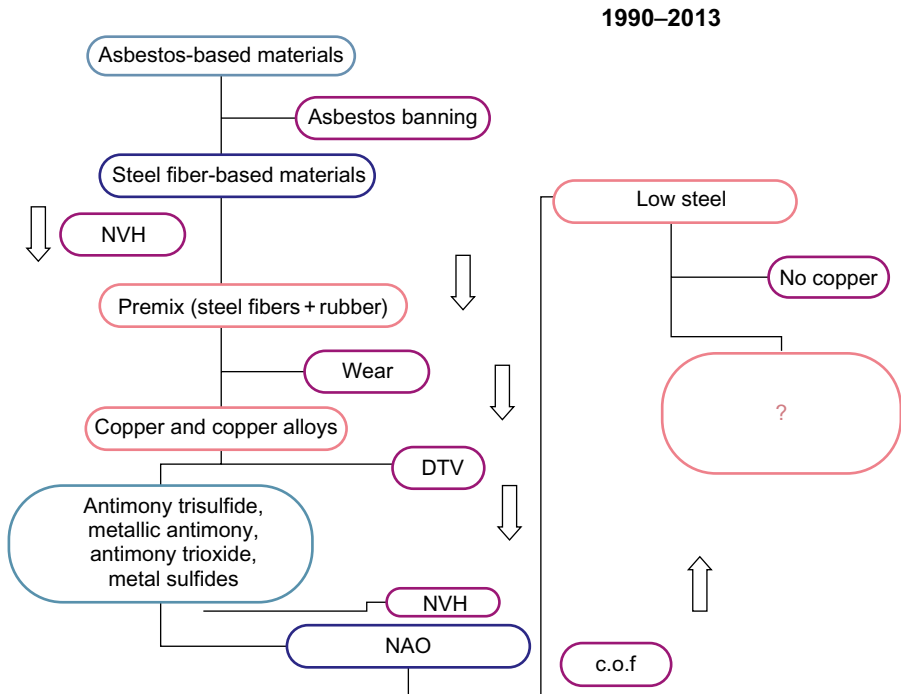


Figure 3.1 Evolution of friction material formulas in the past two decades.

3.2 Organic bound materials

Organic bound friction materials are the most widespread in the world, since they imply a consolidated production process. Their main limit is the thermal decomposition onset of the thermoset. The most commonly used thermosets are phenolic resin. Novolacs are especially popular since they allow the manufacturers to use dry processes, while resoles imply “wet” mixtures accompanied by instability. Nevertheless, dry mixtures may be more easily affected by segregation of particles.

The organic binder's main effect is to create a network that incorporates all the fillers or friction modifiers. The wear resistance depends considerably on the thermal decomposition of the organic binder. Above the onset temperature, the organic binder is decomposed rapidly, even without leaving a carbonized structure due to oxidation which forms CO_2 . Indeed, at high dissipated powers friction material wear becomes exponential.

Apart from incorporating the several components of the friction material, phenolic resins provide good mechanical properties to the final brake pad, including toughness, viscoelasticity which is effective at dissipating mechanical waves (noise), and a certain degree of compressibility, which provides a good pedal feeling if not excessive. Flexural modulus is usually around 10 GPa, and tensile strength around 20 MPa. The strain (compressibility) usually stays between 1% and 2%.

Nevertheless, the other components affect the mechanical properties of the final product, especially fibers, which contribute considerably to creating a resistant structure.

3.2.1 *Formulas*

There are many types of formulas, all of them based on the same concept. Formulas contain a binder, a certain balance of lubricants and abrasives, metals that may be used for several purposes at the same time, such as strengthening the material, increasing the coefficient of friction, dissipating the large amount of heat produced on the friction interface, and so forth. Rubber is mostly added in brake pads to damp vibrations/noise, and to provide a certain grade of compressibility and flexibility in brake linings. It's noteworthy to point out that rubber is not used as a friction material binder. Organic, inorganic, or metallic fibers preferred in pulp form are added to reduce dusting during blend handling, to work as a thermal barrier (such as cellulose, aramid, and rock fibers), and to serve as a structural and strengthening component to decrease wear and increase resistance to fracture during both hot production processes and work. However, the temperature range in which these fibers fulfill their intentional purpose depends on their chemical composition and structure. Sometimes, decomposition of the fiber is wanted to generate a certain porosity on the surface. These kinds of materials were developed mostly empirically, without a clear knowledge of the tribological processes in which they were involved.

In this book the formulas are classified in the following ways. Semimetallic formulas are those that contain metals in a metallic state between 50 and 70 wt.% with steel fiber content equal to or higher than 30 wt.%. Ceramic formulas (also called NAO) do not contain steel fibers, and have a content of nonferrous metals lower than 20%. Low steel formulas have a content of steel fiber lower than 20%. Finally, low metal formulas have a total content of metals lower than 20% including steel fibers. This text will not use the misleading term *hybrid formulas* for low metal ones. Truck (commercial vehicle, CV) formulas can be considered to belong to semimetallic formulas; however, these contain both different lubricants and a different abrasive-to-lubricants ratio than those for passenger cars. All this information is summarized in [Table 3.1](#).

3.2.2 *Semimetallic formulas*

The so-called semimetallic formulas are characterized by a high content of metals, usually exceeding 50% in weight. The metals are steel fibers in great abundance, copper, copper alloys (bronze and brass), and tin and zinc in some cases. The other components are a mixture of strong abrasives and lubricants.

The abrasives used in those formulas are calcined alumina, chromite, among mild abrasives magnesium oxide and clay of the family of kaoline. Lubricants used are natural graphite and synthetic graphite, assisted by sulfurs. Several years ago, in the 1990s, molybdenum disulfide (MoS_2) was very common as well as diantimony trisulfide (Sb_2S_3). Other common ingredients were the so-called friction powder, which is reddish cross-linked cardanol, and premixes composed essentially of rubber and steel fibers. These premixes were very popular during the 1990s, when the change to

Table 3.1 Typical range of lubricants and metals in NAO, low steel, low metal and truck (commercial vehicle, CV) materials

Raw material	Ceramic/NAO (%)	Low steel (%)	Low metal (%)	Semimetallic (%)	Truck (CV) (%)
Lubricants					
Fine graphite	4–9	2–8	4–10	4–10	2–5
Coarse graphite	2–5	0–7	4–8	5–10	2–10
Sulfides					
Sn/Sb sulfides	2–5	2–5	2–5	2–7	2–6
Cu sulfide	2–5	2–5	2–5	2–10	3–6
Other sulfide	0–4	0–4	0–4	2–5	2–4
Ferrous metals					
Steel fibers	0	10–18	5–10	20–35	25–35
Iron powder	0	2–5	1–2	2–7	0–10
Nonferrous metals					
Copper	10–16	6–15	0–6	2–10	12–20
Copper alloys	5–10	5–10	0–5	2–10	6–15
Zinc/Sn	0–4	0–4	0–2	0–4	0–2

asbestos-free materials occurred. They were prepared on the basic idea that coupling rubber, which is a noise damper, to steel fiber will allow the materials to have the benefits of both components: the strength of steel fiber and damping of rubber. The most commonly used rubbers were styrene butadiene (SBR) and chloroprene rubber, which have the possibility of cross-linking for the unsaturated bonds $C=C$. For the preparation of this premix a solvent was used to dissolve the rubber, which incorporates steel fibers after solvent removal by stripping. These kinds of processes were almost completely abandoned in updated industries to eliminate toxic organic solvents such as trichloroethylene. The most common way to prepare this premix is to use dry mixing using mechanical energy to favor the incorporation of steel fiber in the rubber matrix. Most updated materials contain acrylonitrile butadiene rubber (NBR), instead of the aforementioned rubbers. NBR is a more polar rubber than SBR, more resistant to solvents, compatible with the several ceramic compounds of new formulas, more resistant to heat, and can be effectively used without carbon black.

Figure 3.2 shows some typical ratios between the main categories of components: abrasives, lubricants, total metals including steel fibers, nonferrous metals (non fer met), graphite and sulfides for ceramic formulas, low steel and CVs (truck) type or semimetallic formulas. It is noteworthy to point out that the ratio of abrasives to lubricants increases from “truck” formulas to ceramic ones, while ferrous metals, mostly steel fibers and to a minor extent iron powder, decreased. The abrasives of semimetallic formulas are usually strong abrasives such as alumina, and to a minor extent corundum, which must quickly remove the growing oxides on the disk rotor surface, while ceramic formulas need only weak abrasives such as zircon silicate.

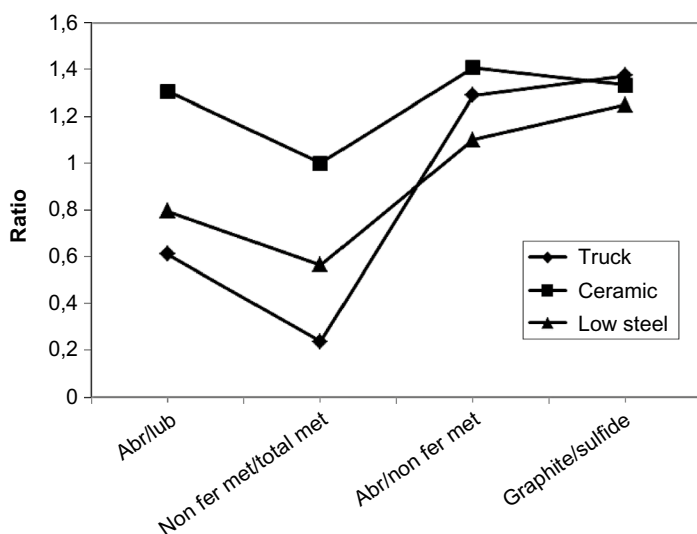


Figure 3.2 Typical ratios between the main categories of components: abrasives (abr), lubricants (lub), total metals (total met), and nonferrous metals (non fer met), graphite and sulfides for truck, ceramic and low steel formulas.

Other kinds of abrasives can be found in recent years, such as metal carbides and silicon carbide. Also chromite, which is a mineral of mixed oxide of iron and Cr(III) ($\text{FeO-Cr}_2\text{O}_3$), is used in low-cost formulas.

3.2.3 *Truck (CV) formulas*

Truck, i.e. CV, formulas follows the scheme of semimetallic ones but sulfides play an important role as well as the coefficient of friction. The density of energy to be dissipated is very high as well as the shear stresses, so the coefficient of friction is preferred to be high. Moreover, the implied thermal–mechanical stresses amplify problems with disks that are present also in passenger cars, such as hot spots. In this case, these problems cause disk thickness variation and consequently vibrations, while in the CV case they can lead to more severe problems such as cracks provoked by the thermal–mechanical stress. These cracks can be either prevented or mitigated through the use of sulfides such as Sn(II, IV) and Sb(III), which contribute to the creation of a tribofilm, improving lubrication and decreasing the uneven wear and stresses. Indeed, another method for decreasing this phenomenon is to use more compressible materials, which adapt to the rotor surface without concentrating stresses in small areas.

In these cases, it is also common to use rock wool and other ceramic pulp, including glass fibers, to increase the mechanical stiffness and act as a thermal barrier. However, these fibers due to the process may form respirable fibers, which are potentially dangerous. There are versions, however, based on magnesium and calcium silicates, which are biocompatible and can be eliminated by the human body.

Truck formulas almost always need an anchoring system additional to phenolic resin-based adhesives to improve the adhesion to the backing plate.

3.2.4 *Low metal*

The low metal formulas are characterized by a low content of all components in the metallic state. Since stick-slip and noise are connected to the presence of metals, the basic idea of these formulas is to increase comfort. However, most of these formulas can be adequate, especially for rear brakes, since their average coefficient of friction is usually lower than that of the more metallic formulas. Indeed, their coefficient of friction is around 0.35–0.38, while semimetallic formulas are around 0.4.

This kind of formula works with a different concept of the tribofilm, which is more of a composite of several oxides, not only the dominant magnetite. For example, fine particles of zircon silicate are incorporated in the oxide tribofilm. The content of resin is larger 1–4 wt.% than that of semimetallic formulas. Round shaped particles are also used to reduce wear due to abrasion. Low wear is pursued using fine abrasives instead of coarse particles. It is well known that the size of the abrasive affects wear rate. Thus, silicon carbide is introduced in this type of formula instead of corundum because it is less aggressive due to the silicon oxide film covering the silicon carbide particles, and it is used with particles usually under 45 μm , as was demonstrated for

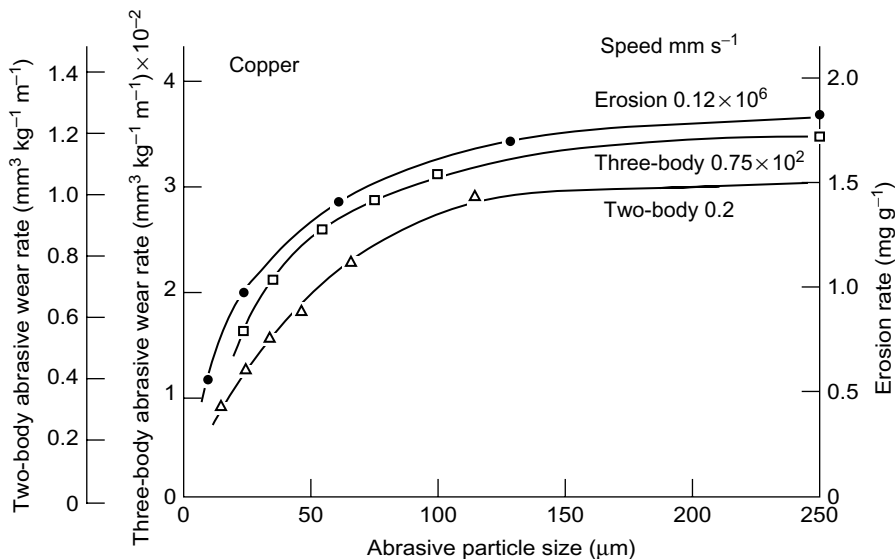


Figure 3.3 Wear rate of copper under conditions of two-body, three-body abrasion, and erosion by silicon carbide particles of different size.

A. Misra, I. Finnie, *On the size effect in abrasive and erosive wear*, *Wear* 65 (1981) 359–373.

other applications with a copper counterpart instead of the classical gray cast iron for brakes [2] and as shown in Figure 3.3.

The structure of the semimetallic formula can be described as follows: fillers have considerable importance, although not similar to that of ceramic materials. The term *filler* is very generic but, with this, we can speak about soft inorganic or ceramic materials such as barite (BaSO_4), fluorite (CaF_2), calcium carbonate (CaCO_3), etc.

A typical formula is given in Table 3.2. The amount of the binder depends on the process used and can be between 5 and 15 wt.%. The lower amount corresponds to hot positive molding with a unitary mold. In this case, the control of real pressure and temperature in the mold allows higher quality to be achieved and less binder to be used. Many times a large amount of binder is used to minimize the variability of the process parameters. A higher amount of resins (binder) corresponds to hot negative molds, which cannot achieve uniform pressure and temperature. An inadequate level of resin often leads to cracks in the process or field use or to high friction material wear.

The remainder of the formula does not depend on the process but only on performance, i.e., coefficient of friction and wear.

There are many variants of the formula of Table 3.2. Most of them are focused on cost reduction, which is one of the main current concerns. Usually the expensive raw materials are substituted with cheaper products leading to lower performance in many cases. For example, silicates such as kaolin and garnet substitute for the expensive zircon silicate. Other formulas are based on different concepts, such as the following one in Table 3.3, which overturns the basic concept that fillers do not play a fundamental role.

Table 3.2 A typical low metal formula

Raw material	Weight percent (wt.%)
Binders	
Novolac with high flow (45–60 mm)	5
Novolac with short flow (10–20 mm)	2
Fibers	
Aramid fiber	2
Cellulose fibers	1.6
Dampers	
NBR	3
Abrasives	
Silicon carbide	0.4
Zircon silicate	10
Lubricants	
Fine graphite (<45 µm)	2
Coarse graphite	10
Sulfides	
SnS	3
Chalcopyrite	3
ZnS	6
Nonferrous metals	
Bronze powder	3
Brass chips	2
Copper powder	5
Ferrous metals	
Steel fiber	10
Sponge iron	2
Fillers	
Barite BaSO ₄	15
Calcite CaCO ₃	10
Fluorite CaF ₂	5

3.2.5 Low steel formulas

Low steel formulas are similar to low metal formulas. The higher steel fiber content makes it more suitable for a front axle due to the higher coefficient of friction. They usually need fewer abrasives than low metal formulas and a damping system able to minimize the negative effects of steel fiber on noise and vibrations. This damping

Table 3.3 Example of a different concept of low metal formula

Raw material	Weight percent (wt. %)
Binders	
Novolac with high flow (45–60 mm)	10
Novolac with short flow (10–20 mm)	2
Fibers	
Cellulose fibers	2
Polyacrylonitrile fiber	2
Dampers	
NBR	2
Abrasives	
Chromite $\text{FeO} \cdot \text{Cr}_2\text{O}_3$	8
Lubricants	
Fine graphite (<45 μm)	6
Coarse graphite	6
Sulfides	
SnS	4
ZnS	6
Ferrous metals	
Steel fiber	10
Sponge iron	2
Fillers	
Calcite CaCO_3	20
Fluorite CaF_2	20

system may require the use of premix with rubber and lubricant, as in semimetallic materials. In this type of formula MgO is sometimes used as a mild abrasive to stabilize the coefficient of friction. This stabilization can be achieved with the right balance between growth and destruction of the oxide tribofilm as previously discussed. On the contrary, when there is only a source of iron, the equilibrium of the composite tribofilm is still more critical in order to have a steady coefficient of friction.

An interesting study executed by Kumar and Bijwe [3] depicts the role of metals in friction materials without correlating with a mechanism. The study was focused on steel fiber, brass fiber, and copper powders introduced in a non-asbestos formula balancing the total content with barite and keeping the remaining components of the formula constant. The metal content was investigated on two levels, 10 and 20 wt.%. The tribological results showed that the main effect of these metals is to decrease the fading of the coefficient of friction due to either speed or load increasing. For example, in [Figure 3.4](#) the effect of speed on the coefficient of friction is shown.

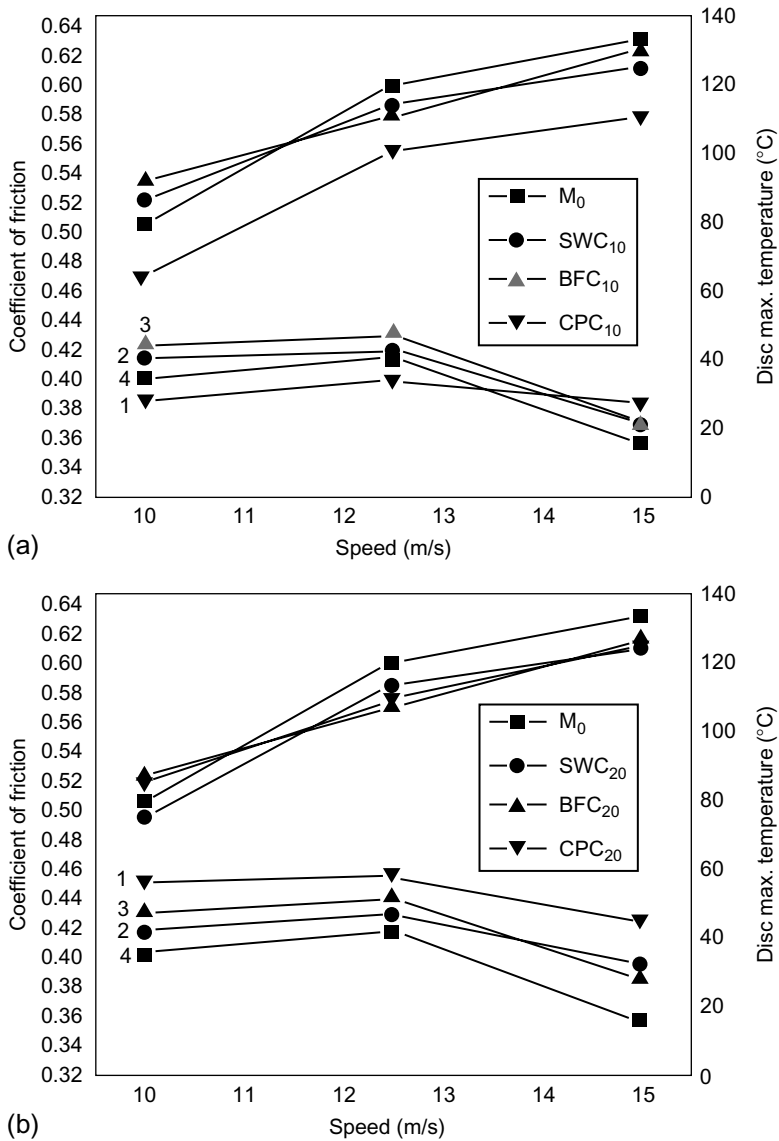


Figure 3.4 Effect of speed on different friction materials with different metals and content 20 wt.%, as determined in a pad-on-disk tribometer. M_0 , reference material without metals; SWC, steel wool; BFC, brass fiber; CPC, copper powder. The subindex 20 indicates that the amount of metal is 20 wt%.

A. Misra, I. Finnie, *On the size effect in abrasive and erosive wear*, *Wear* 65 (1981) 359–373.

In Figure 3.4, it is possible to observe that the lowest decrement of the coefficient of friction with increasing speed was found for copper powder with the content of 20 wt.% and the highest for M_0 which did not contain metals. The stabilizing effect provided by metals is the true challenge of working with few metals as in low metals formulas. This challenge has been faced by using materials which work as heat sink materials.

Wear of friction materials is also strongly influenced by metals, but the general thinking that they improve it can be true only in a certain extent.

In the cases discussed in Figure 3.5, the only material with a lower wear than the reference (without metals) in both conditions (load and speed tests) is that with 10 wt.% of copper, while the material with 20 wt.% exhibits more than double the wear volume. The wear increment due to higher metal content is very marked with copper and its alloys, more so than for steel fiber. In this regard, it should be remembered that steel fiber contributes considerably to the material strength. On the other hand, since pure copper is a metal with high thermal conductivity ($401 \text{ W m}^{-1} \text{ K}^{-1}$), an excessive transfer of heat towards the pad favors the weakening of the binder in the proximity of the material surface, finally causing a wear increment.

The comparison of the surface by scanning electron microscopy of three materials, M_0 (without metallic components), CPC10 (10 wt.% of Cu powder), and CPC20 (20 wt.% of Cu powder), reveals that there are significant topographical and morphological differences, which are correlated with the fading of the coefficient of friction and wear rate [3].

The surface of the CPC10 material exhibits clear plateaus, corresponding to the junction, made of recycled debris according to the mechanism described in Chapter 2 (Figure 3.6). However, the plateaus are not very extensive since the wear debris are much less than in the other cases having low wear rate. In addition, the microstructure of the friction material that covers the largest area seems relatively intact, meaning that the binder is still working. The surface of M_0 exhibits a large plateau of composite oxides, and some detachments occurred. This extended oxide tribofilm is the main

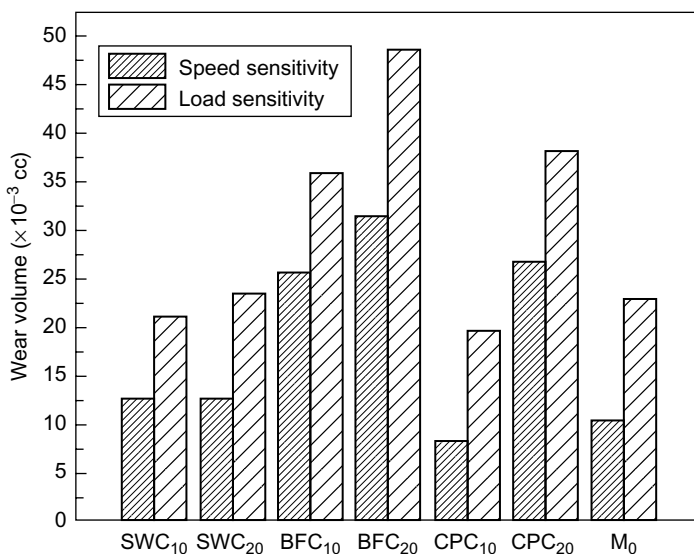


Figure 3.5 Cumulative wear behavior of the selected composites in two testing modes viz. speed sensitivity and load sensitivity. Load sensitivity: 2, 3, 4 MPa; speed: 12.5 ms^{-1} ; speed sensitivity: 10.0, 12.5, 15.0 ms^{-1} ; load: 3 MPa.

M. Kumar, J. Bijwe, *Role of different metallic fillers in non-asbestos organic (NAO) friction composites for controlling sensitivity of coefficient of friction to load and speed*, Tribol. Int. 43 (2010) 965–974.

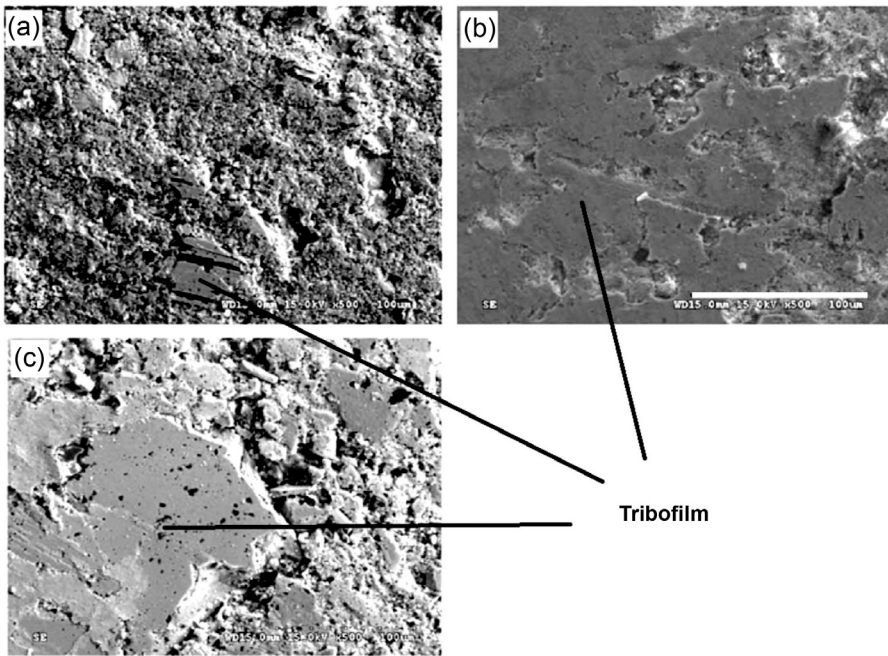


Figure 3.6 SEM images: (a) CPC10 (low wear, low fade), (b) M_0 (high fade, reference), and (c) CPC20 (high wear, lowest fade).

M. Kumar, J. Bijwe, *Role of different metallic fillers in non-asbestos organic (NAO) friction composites for controlling sensitivity of coefficient of friction to load and speed*, *Tribol. Int.* 43 (2010) 965–974.

cause of the coefficient of friction decay with increasing speed or load, because the coefficient of friction between oxide surfaces is generally lower than that between metallic surfaces. It is noteworthy to point out that also the disk is covered with an oxide tribofilm. CPC20 exhibits a rough surface with a large plateau of secondary junctions (made of oxidized wear debris) and particles of raw materials emerge in the large areas where detachment occurred. This may indicate that binder failure due to the excessive heat transfer towards the friction material caused a large removal of particles and formation of oxidized/oxide wear debris that finally formed the layer. Nevertheless, the fresh metals emerging from craters preserve a high coefficient of friction.

In summary, the low steel materials are less subject to a strong sensitivity to speed and load than are low metal ones, and for these characteristics are more suitable for front axle applications. The true performance challenge is represented by low metal and the so-called ceramic materials.

3.2.6 Ceramic formulas

The description of ceramic formulas is now going to evolve in respect to what was presented in Table 3.1. These materials require copper to favor heat dissipation since

they do not contain steel fiber, which is a common ingredient in the other materials and contributes to the whole thermal conductivity. The restraint to use copper in the United States for automotive friction materials, as well as the price fluctuations, is forcing a move towards materials with a different conceptual design, since it is almost impossible to think of suitable materials absolutely without metals. Indeed, metals, apart from their effects on the coefficient of friction, contribute considerably to the heat transfer from the friction interface towards the pad and the right balance must be struck. Low metal materials are the alternative to this difficult situation in the meantime. A typical ceramic formula is shown in [Table 3.4](#).

Table 3.4 Example of ceramic formula

Raw material	Weight percent (wt.%)
Binders	
Novolac with high flow (45–60 mm)	12
Novolac with short flow (10–20 mm)	3
Fibers	
Aramid fiber	2
Ceramic fiber	2
Dampers and organic compounds	
NBR	3
Black friction powder	2
Abrasives	
Zircon oxide (ZrO_2)	3
Silicon carbide ($<15\ \mu\text{m}$)	1
Magnesium oxide (MgO)	8
Potassium titanate (hexa-octatitanates) $\text{K}_2\text{O} \cdot x\text{TiO}_2$ $1 < x < 8$	10
Lubricants	
Fine graphite ($<45\ \mu\text{m}$)	2
Coarse graphite	8
Sulfides	
SnS , SnS_2 or WS	4
ZnS	5
Nonferrous metals	
Copper fiber	7
Brass chips	4
Fillers	
Fluorite CaF_2	16
Petroleum coke	8

These kinds of materials usually combine strong and mild abrasives with the purpose of wearing the disk surface to produce enough iron debris to create a composite tribofilm with adequate friction level. As in most cases, in friction materials the trick is to find the right balance among opposites. Ceramic materials are reinforced by ceramic fibers such as Ca–Mg silicates, rock wool, and fibrous titanates. Historically, they contain a certain amount of potassium titanate, which was initially introduced to compensate for the steel fiber removal from ceramic formulas for its fibrous nature.

The basic idea was that another fiber should be substituted for a fiber, to keep a similar mechanical strength of the materials. Nevertheless, a ceramic fiber implies less thermal conductivity and hence less heat removal from the interface. However, after questioning and pointing out the possible health risks and danger connected to any kind of respirable fibers, many companies are trying to substitute other ceramic materials for potassium titanate. To avoid having to develop totally new formulas, there have been several attempts to develop nonfibrous potassium titanates.

The attempts to increase thermal conductivity through certain ceramic materials such as silicon carbide have not been successful, because these nonoxide ceramics are covered by a thin oxide layer with totally different thermal characteristics, such as silicon oxide (SiO_2). Moreover, silicon carbide exhibits polymorphism and each type (usually identified as α and β) has a different structure and different thermal properties. It should be noted that silicon carbide is a strong abrasive (Mohs hardness 9) and cannot be used in large amounts without seriously affecting wear of both friction parts.

However, as is typical in friction materials, a balance of properties is searched for, and it is possible to combine ceramics with low thermal conductivity, such as zirconia, with those with higher thermal conductivity, such as silicon carbide and magnesium oxide (see Figure 3.7). In any case, the thermal conductivity decreases with increasing temperature in a nearly exponential manner for ceramics, eliminating their contribution, as shown in Figure 3.6 [4,5].

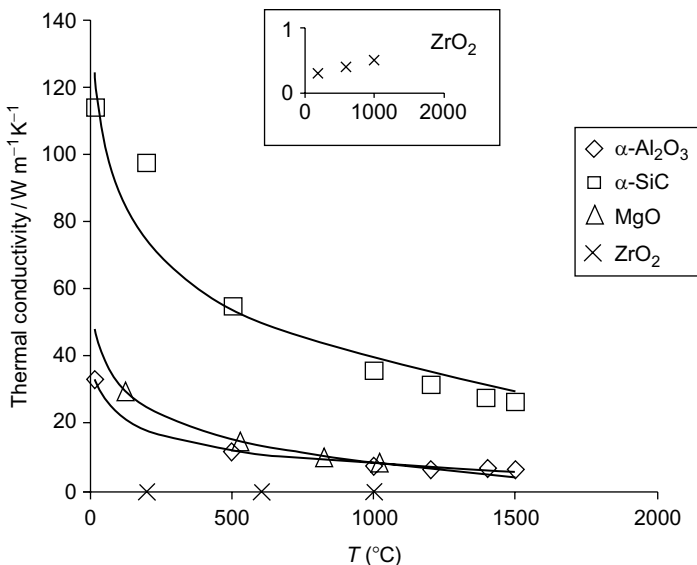


Figure 3.7 Thermal conductivity of some ceramic materials [4,5].

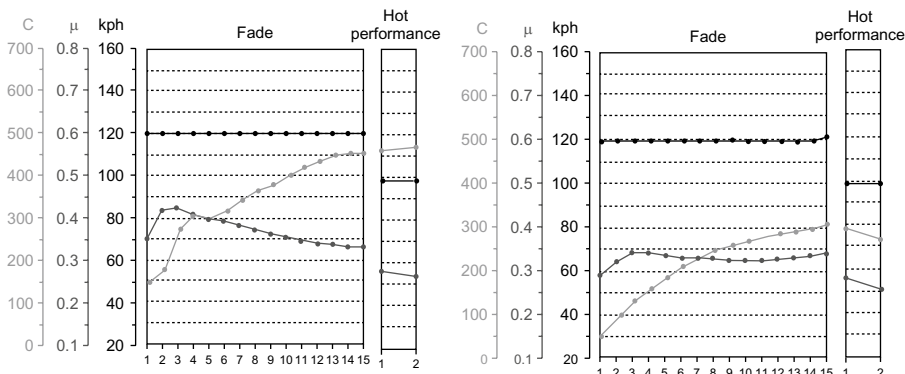


Figure 3.8 Right: material with Cu (8 wt.%) and Sb_2S_3 (3.6 wt.%). Left: material without Cu and Sb_2S_3 (SAE J2430).

P.W. Lee, P. Filip, *Friction and wear of Cu-free and Sb-free environmental friendly automotive brake materials*, *Wear* 302 (2013) 1404–1413.

Metals can contribute more to thermal conductivity of the ceramic materials, especially copper, which has a thermal conductivity between 385 and $353 \text{ W m}^{-1} \text{ K}^{-1}$ in the temperature interval between 20 and 600°C , and aluminum, between 200 and $250 \text{ W m}^{-1} \text{ K}^{-1}$ in the temperature interval between 20 and 200°C . Steel used in friction materials has a thermal conductivity around $75 \text{ W m}^{-1} \text{ K}^{-1}$, much lower than that of copper but higher than most ceramics. Brass (70% Cu, 30% Zn) and bronze (75% Cu, 25% Sn) have a thermal conductivity around 100 and $25 \text{ W m}^{-1} \text{ K}^{-1}$. This may explain the reduced performance on fading of brass fibers.

The use of metallic aluminum is not very common since it is quickly oxidized on the surface, forming a thermal barrier film, and may give strong reactions in different phases of the process. Lee and Filip underlined the role of metals, especially Cu and Sb as sulfide, into building the friction layer of brake pads [6]. They attributed the lower wear of both disk and pads to this friction layer, and a lower coefficient of friction of the material with Cu and Sb_2S_3 . However, they also found a more marked fading for the friction materials without the two metals, in accordance with the results found by Kumar and Bijwe [3], as shown in Figure 3.8.

This study shows clearly that the more “ceramic” material caused a temperature increment much higher than that of the Cu-free and Sb-free materials. Between the final temperature of the material with Cu and the Cu-free and Sb-free, there is a 150°C difference during the fading test of the SAE J2430. Although the full role of tribofilm is not yet well known, the dissipation and heat transfer exerted by metals on the friction interface is well documented.

3.3 Carbon–ceramic rotors and friction materials

For many years the technical evolution in rotor materials was related just to gray cast iron and steel. The few innovations concerned only the passage from solid to ventilated disks for the front axle. The efforts to decrease the vehicle mass also implied an attempt to reduce the brake mass, either by using low density metals or carbon and

ceramic materials. Rotors made of aluminum and ceramic fillers (Cer-mets, metal matrix composites) by means of powder metallurgy, although the production method was well established, performed poorly, especially as regards temperature increment, considering the limiting factor of the aluminum melting point (660°C). Carbon–carbon (CC) materials are currently used for aircraft brakes, both rotors and pads, and racing cars. They have the advantage of low density (one-fifth of iron density, which for gray cast iron is around 7.6 g cm^{-3}) and high heat capacity. However, their coefficient of friction is unstable and depends too much on temperature and humidity. Their production process is very expensive, since it requires a very slow step of densification of the carbon matrix.

A new class of friction materials was developed in the last decade: the carbon–ceramic materials, specifically, carbon/carbon–SiC (C/C–SiC), with a low density around 2 g cm^{-3} . These materials are currently used for rotors of top-class cars such as the Audi 8 and 911 Turbo Porsche, since they are more expensive than standard gray cast iron rotors but more accessible than carbon–carbon materials [7]. There are three main processes to make these rotors: (a) a process essentially based on Si infiltration by chemical vapor deposition, in this case called *chemical vapor infiltration* (CVI); (b) instead of infiltration from a gas phase, this process involves an impregnation of a slurry followed by sintering at high pressure—this method is also called a *high-pressure sintering process* (HP-sinter); (c) a process in which liquid silicon is used to infiltrate the carbon matrix, called *liquid silicon infiltration* (LSI). All these methods share the following phases: the fabric preform preparation, the infiltration with a resin in liquid state, the pyrolysis/carbonization process of the composite fiber-resin material (also called polymer impregnation and pyrolysis (PIP)), the infiltration with silicon (with different methods), and the formation of SiC.

A schematic representation indicating these phases for the LSI is presented in Figure 3.9.

The preform usually has a density of about 0.60 g cm^{-3} , while the carbon fiber reinforced plastic density is around 1.5 g cm^{-3} , and the final material after Si infiltration and SiC formation has a density around 2.4 g cm^{-3} , with a low porosity around 2%. The microstructure of the final composite material is shown in Figure 3.10.

The cloth parallel to friction favors the formation of the friction film, while the needle fibers favor thermal exchange from the surface to the bulk.

The final composition of the composite material is 54 wt.% carbon, silicon carbide 40 wt.%, and residual silicon around 6 wt.%.

3.3.1 Mechanical and friction performances of C/C–SiC

The C/C–SiC materials exhibit mechanical properties that make them suitable for brake applications. The mechanical characteristics of these materials are anisotropic, since there are significant differences in the parallel and perpendicular directions to the sliding surfaces. Cracks always begin in the matrix in flexural tests, propagate following the fiber direction, and finally fiber bundles are pulled out. Exposed fibers, which bear all the load after matrix failure, yield with the consequent destruction of the composite. In the flexural tests the material exhibits a pseudo-plastic behavior

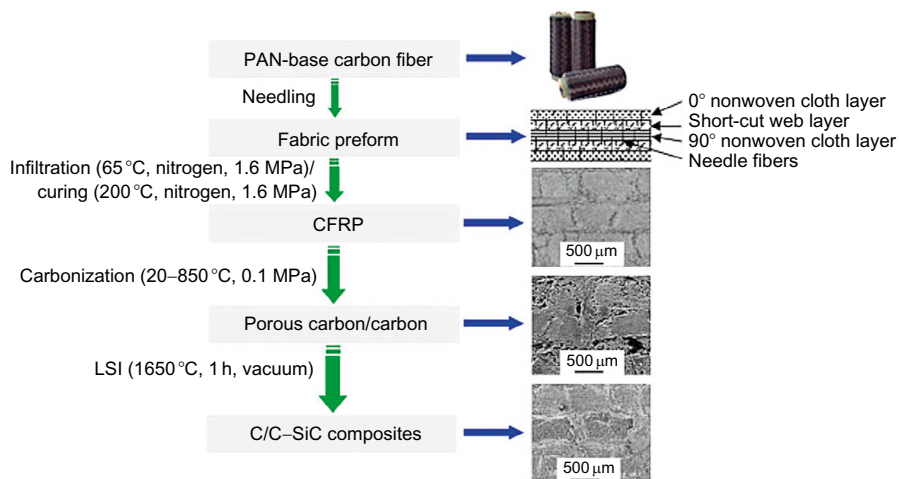


Figure 3.9 Schematic representation of manufacturing process for C/C-SiC composites.

CFRP: carbon fiber reinforced plastic.

P. Xiao, Z. Li, X. Xiong, *Microstructure and tribological properties of 3D needle-punched C/C-SiC brake composites*, *Solid State Sci.* 12 (2010) 617–623.

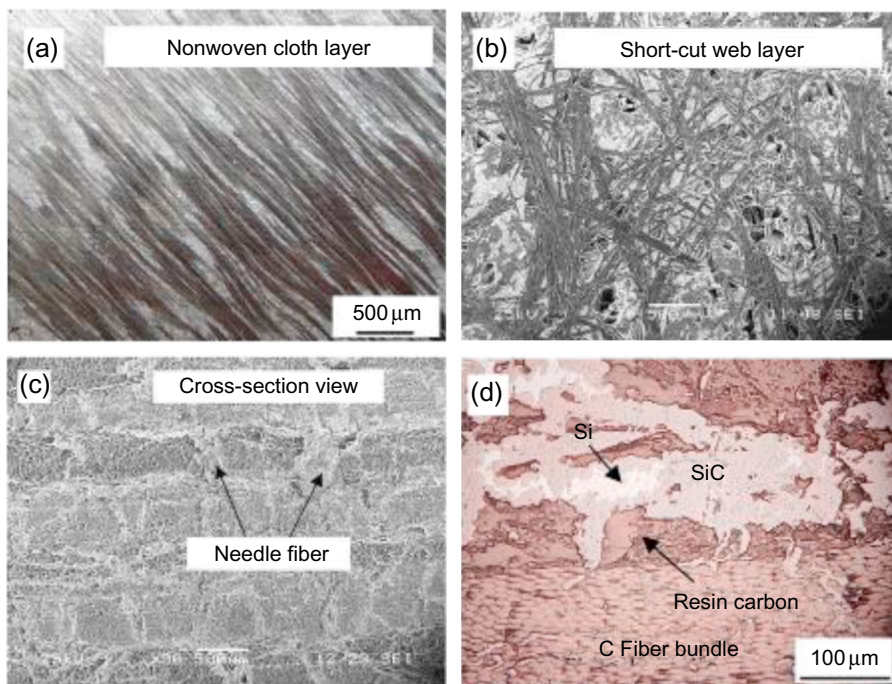


Figure 3.10 Microstructure of the C/C-SiC composite: (a) nonwoven fiber cloth, (b) short-cut fiber web, (c) needle fibers, and (d) the different components of the final material.

P. Xiao, Z. Li, X. Xiong, *Microstructure and tribological properties of 3D needle-punched C/C-SiC brake composites*, *Solid State Sci.* 12 (2010) 617–623.

Table 3.5 Mechanical properties of C/C–SiC composites

Flexural strength (MPa)	⊥	174±22
	=	134±31
Compressive strength (MPa)	⊥	241±45
	=	188±36

“=”: direction parallel to the sliding surface, “⊥”: direction perpendicular to the sliding surface.
Z. Li, P. Xiao, X. Xiong, B. Huang, *Preparation and tribological properties of C fibre reinforced C/SiC dual matrix composites fabrication by liquid silicon infiltration*, *Solid State Sci.* 16 (2013) 6–12.

without a sharp load fall. In compression tests, in the perpendicular direction both matrix and fibers bear the load and cracks cross both frameworks. In this case, the behavior is elastic till the drop fall of the material failure. An example of the mechanical properties of a C/C–SiC composite is reported in Table 3.5 [8]. It should be noticed that the strength of the direction perpendicular to the sliding surface is considerably higher than the parallel one due to the contribution of both matrix and fiber frameworks to the mechanical resistance.

Among the different types of C/C–SiC products, there are significant differences that are caused by the production process and depend on the final composition and porosity. In Table 3.6 the main tribological characteristics of different types of C/C–SiC products, which were obtained by means of pin-on-disk tribometer with self-mating surfaces, are reported and compared with a CC material elaborated for aircraft brakes and made through isotherm–isobar chemical vapor infiltration (I-CVI). The tribo-tests' applied load was 3.5 MPa, the sliding speed was 0.3 ms^{−1}, the temperature varied from 20 to 400 °C. The tests were carried out in air with relative humidity varying from HR=0% (dry air) to HR=60%. The samples were basically obtained with three process techniques: I-CVI or pulsed CVI (P-CVI) by alternating carbon and silicon infiltration, PIP followed by LSI. In the latter case, the pyrolytic carbon densification was carried out with toluene, and silicon was deposited from the vapor phase with methyltrichlorsilane. The volume of carbon fibers in the five tested samples was 25% [9].

The results of Table 3.6, which concern tribometric tests, show that the C/C–SiC products exhibit a higher wear rate than CC materials, although, in general, they exhibit a higher coefficient of friction than CC materials at low temperatures. There is still a large margin for improvement of the production process in order to achieve lower wear rates and a more stable coefficient of friction.

3.4 Railway

A great variety of materials are used for railways; this was true especially after high-speed trains began to be widespread. The basic materials are cast iron shoes that apply on the train wheels. Organic composite materials have certain uses for disk brake pads, substituting for gray cast iron shoes, and especially in disk brake pads for standard trains. However, metal sintered materials have become very common

Table 3.6 Composition and tribological behavior of the samples of C/C–SiC compared with a CC sample

Composite (vol.% SiC/Si)	Method	Density (g cm ⁻³)	Porosity (vol.%)	Coefficient of friction		Wear (μgm ⁻¹ MPa ⁻¹)	
				20 °C	400 °C	20 °C	400 °C
CC (–/–)	I-CVI	1.75	12	0.05–0.10	0.30–0.40	≤0.8	≈12
C–(C–SiC) ₇ (31%/–)	P-CVI	1.90	13	0.20–0.25	0.60–0.65	≈10	≈500
C/C–SiC–Si (10%/20%)	PIP-LSI	2.06	6	0.10–0.15	0.55–0.70	≈1.5	85–260 = f(RH)
C/C–SiC (57–63%/–)	I-CVI	2.34	12–18	0.35–0.45	0.55–0.70	≤1.5	≈85
C/C–SiC–Si (54%/17–18%)	I-CVI + LSI	2.60	3–4	0.15–0.60	0.80–1.60	0.7–4.0	≈25

S. Fouquet, M. Rollin, R. Pailler, X. Bourrat, Tribological behaviour of composites made of carbon fibres and ceramic matrix in the Si–C system, Wear 264 (2008) 850–856.

in the last decades. This type of pad is generally made of separated material blocks because of the limited size of the sintered blocks, which are riveted on the backing plates. In addition, the separated cylindrical blocks allow air to flow among the different sectors, favoring easier cooling of the pad. In organic composite brake pads, a similar effect is obtained through deep cuts, which separate the pad into several sectors.

3.4.1 Sintered materials

The sintered materials for railway applications can be classified into two main categories: copper matrix and iron matrix. Both matrixes need an inert atmosphere for the thermal sintering process (nitrogen is the most frequently used inert gas). The main difference between an organic matrix and a metal sintered matrix is the decomposition (or failure) of the binder. Phenol formaldehyde resins begin to decompose from 350 to 400 °C, while Cu matrix melts at 1085 °C and Fe matrix at 1538 °C. The thermal stability of the metal sintered materials is considerably higher than that of organic binders.

The production process is usually divided into the following phases: (i) blending of the components; (ii) molding at high pressure (100–200 MPa); (iii) a thermal treatment in nitrogen flux (600–700 °C for Cu matrix; 1000–1200 °C for Fe matrix). During the different phases, size changes may occur for thermal expansion. Nevertheless, these size changes can be quantified exactly, and there are simple techniques used especially to prevent the expansion along the direction perpendicular to the friction interface, such as carrying out annealing in furnaces in which a load is applied to the friction surface of several pads by means of a mobile flat bed.

The reason for using metal sintered materials is briefly indicated by the high density of energy dissipated in train braking applications. The frictional heat of 0.44 kW cm⁻² is dissipated in the interface between the wheel and shoe in a train braking traveling at the speed of 120 kmh⁻¹ [10]. This high heat density requires a matrix able to resist it and an efficient heat dissipation by means of materials with high thermal conductivity, high specific heat, or by means of an efficient cooling design.

Figure 3.11 reports the ranges of the density of power dissipated for different applications with the corresponding type of binder. The higher the power density, the higher is the temperature which the binder has to resist without either decomposing or melting and the heat to be absorbed.

A formulation for sintered copper materials is reported in Table 3.7. It should be noticed that the formulas for sintered materials are simpler than those for organic binders, since in the latter many compounds are aggregated to increase performance at high interface temperatures.

The metal sintered materials have a high density, which is contrary to the current trend to reduce vehicle weight, and the large metal content make them useless for passenger cars for noise reasons. They are widely used for motorcycles because they can balance the low thickness required by the motorcycle brake disk with low wear.

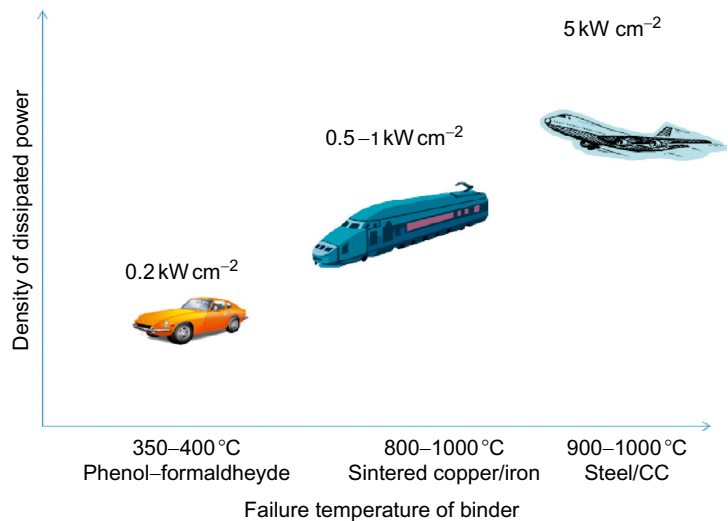


Figure 3.11 Density of dissipated power for different applications: passenger cars, trains, and aircraft.

Table 3.7 A formula of a precursor of metal sintered friction materials

Raw material	Weight percent (wt. %)
<i>Binders</i>	
Novolac with low flow (20–30 mm)	5
<i>Abrasives</i>	
Zircon silicate (ZrSiO_4)	6
Silicon carbide ($<15\text{ }\mu\text{m}$)	1
<i>Lubricants</i>	
Fine graphite ($<45\text{ }\mu\text{m}$)	5
<i>Sulfides</i>	
SnS_2	1
<i>Nonferrous metals</i>	
Dendritic copper	71
Tin	7
<i>Ferrous metals</i>	
Sponge iron	4

3.5 Aircraft

Aircraft friction materials are thought to dissipate high power densities, as shown in Figure 3.11. These levels can be handled only with iron sintered materials, C–SiC or carbon–carbon (CC) materials to provide a high and steady coefficient of friction as well as an adequate thermal stability of the material. A brief outline of CC materials is provided in the following section.

3.5.1 Carbon–carbon materials

CC materials are used for heavy duty applications in brakes. This choice is based upon the high strength of carbon materials at high temperatures over 1500 °C. Their mechanical strength increases with temperature in contrast to most materials based on either a metallic or ceramic matrix (see Figure 3.12) [11]. Moreover, they result in a weight savings of several hundreds of kilograms on an aircraft, in comparison with iron-based materials. They are almost insensitive to thermal shock and mechanical fatigue. CC materials beat all records for endurance, increasing the longevity of the brake disks and lengthening the intervals between replacements. The final result is a lower operation cost of the aircraft, doubtless an important economical criterion for airlines and aircraft manufacturers. However, CC materials are produced through a slow production process and, mainly for this reason, they are still quite expensive.

They are produced through a pyrolysis of a preform, made of carbon fibers arranged in various directions, and organic polymers (e.g., thermosetting resins such as novolacs) followed by a slow and complex densification process. The densification of the porous pyrolyzed matrix is achieved through CVI, by means of hydrocarbons such as methane, propane, toluene, etc. as carbon carriers, or through liquid infiltration by means of liquid

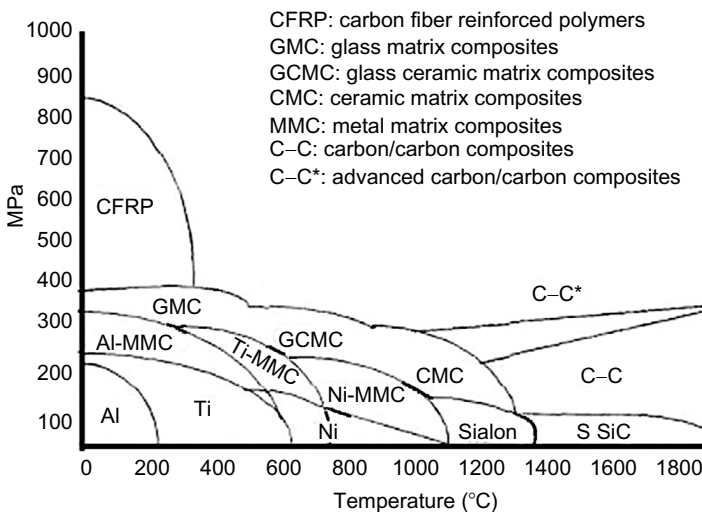


Figure 3.12 Variation of strength of some engineering materials with temperature.

L.M. Manocha, High performance carbon–carbon composites, Sadhana 28 (2003) 349–358.

resins or pitch with or without pressure. The CVI process requires high temperatures between 1000 and 1400 °C and the graphitization even higher temperatures between 1500 and 2700 °C. The cycles of CVI, pyrolysis, and graphitization may be repeated several times to reach the desired density. These cycles are necessary to restore the flow of gases by means of a rearrangement of the deposited carbon by high temperature graphitization, because external pores tend to be closed by carbon deposited by hydrocarbon cracking, which prevents further penetration of gaseous hydrocarbons to densify the matrix. Indeed, the highest densities are achieved by means of intermediate graphitizations and by high-pressure pyrolysis of previous liquid infiltration of pitch/liquid resin (Figure 3.13). CC density and properties depend on the type and volume fraction of reinforcement, matrix precursor used, the heat treatment temperature, etc. Composites made with thermosetting resins as matrix precursors exhibit low densities of 1.55–1.75 g cm⁻³ and well-distributed microporosity; those made with pitch as the matrix precursor, after densification exhibit densities of 1.8–2.0 g cm⁻³ with some mesopores; and those made by the CVI technique with hydrocarbon gases possess intermediate densities and matrices with close porosities.

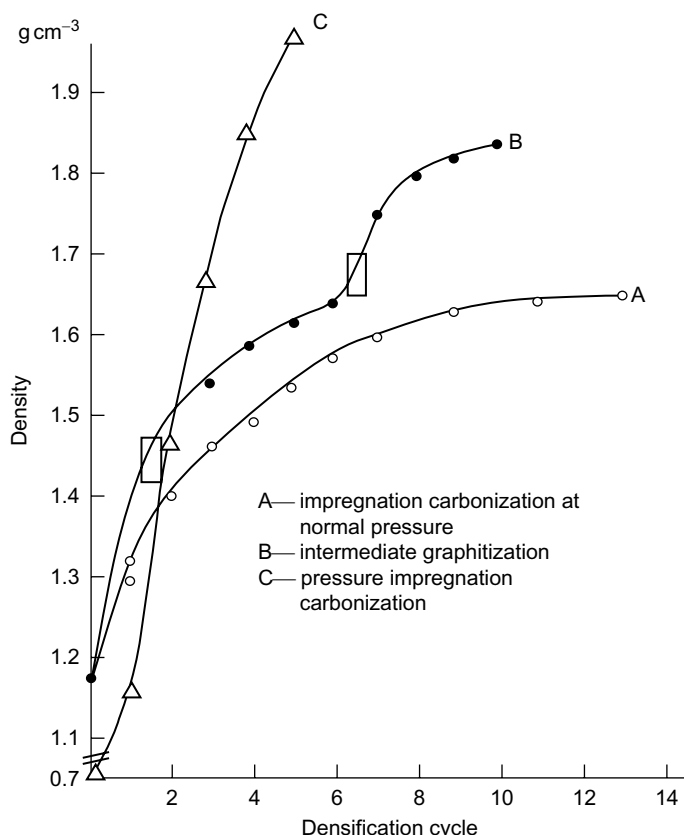


Figure 3.13 Increase in density of carbon–carbon composites with densification.

L.M. Manocha, High performance carbon–carbon composites, Sadhana 28 (2003) 349–358.

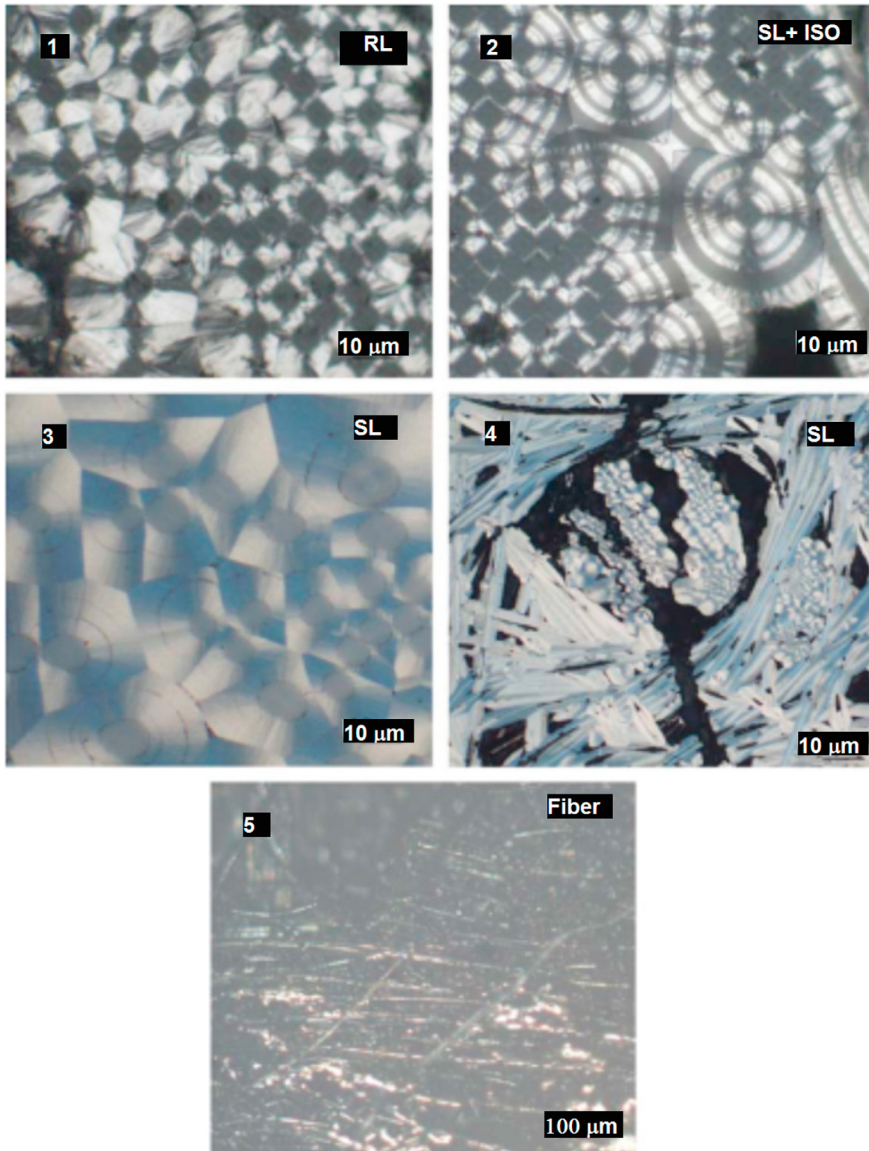


Figure 3.14 The polarized microstructure of pyrocarbon at the radial cross section of a partially infiltrated preform. 1) rough laminar pyrocarbon RL, 2) combination of smooth laminar and isotropic SL-ISO pyrocarbon, 3) and 4) smooth laminar pyrocarbon SL, 5) a carbon fiber where pyrocarbon was not yet infiltrated.

J. Zhao, K. Li, H. Li, C. Wang, The influence of thermal gradient on pyrocarbon deposition in carbon/carbon composites during the CVI process, Carbon 44 (2006) 786–791.

The former (resin-based) composites exhibit high flexural strength, low toughness, and low thermal conductivity, whereas the latter (pitch- and CVI-based) can be made with very high thermal conductivity ($400\text{--}700\text{ W m}^{-1}\text{ K}^{-1}$) in the fiber direction.

The CVI method is the most frequently used for CC aircraft brakes.

Commercially, many stacks of parts are isothermally heated and densified in large furnaces. In commercial CC brake pads, carbon fiber fabric plies are used with fiber tows inserted in the third direction and pitch/CVI route for densification.

Three microstructures are identified by optical microscope in CC materials: smooth laminar (SL), rough laminar (RL), and isotropic (ISO). Unlike SL and ISO, RL materials exhibit high anisotropy, as well as both high density and electric conductivity. In CVI methods, the SL $\rightarrow$ RL transition can be induced by higher temperatures and gas residence time increase [12].

The three microstructures, as well as combinations of them, are shown in Figure 3.14. Zhao et al. carried out a series of experiments in a gradient CVI furnace by Joule heating, in which the temperature in the deposition zone was constant as its position moved outwards the heat source, while graphitization continued inward for a whole process of 160 h [13]. Moreover, Figure 3.15 shows the presence of a determined microstructure depends on the temperature, which is a function of the distance from the heat source; also, the temperature and gas pressure gradient favor heat flow and gas flow towards the deposition zone. The steep temperature and density gradients are in the narrow deposition zone, where all the chemical reactions are occurring. The complicated heat and mass exchanges are located in the porous preform region. It is possible to identify the position of the different types of microstructures (1: RL, 2: SL + ISO, 3: SL, 4: SL, 5: fiber net). The deposition zone corresponds to the first SL zone, and CF corresponds to a carbon fiber zone without deposition [13].

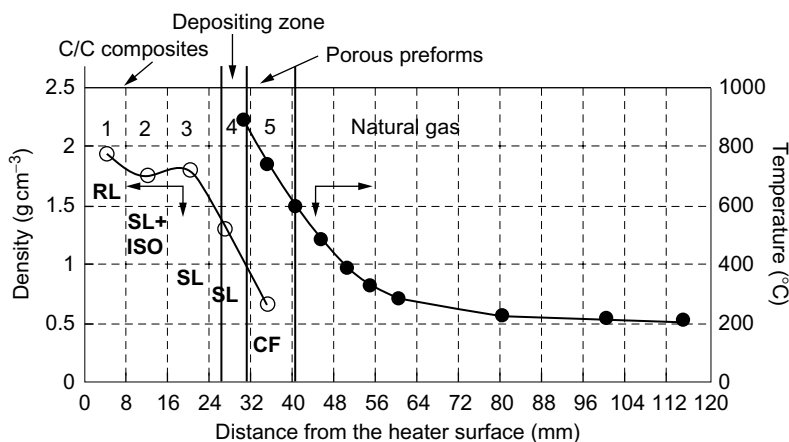


Figure 3.15 The radial direction distribution profile of the temperature and density in the thermal gradient CVI process.

J. Zhao, K. Li, H. Li, C. Wang, *The influence of thermal gradient on pyrocarbon deposition in carbon/carbon composites during the CVI process*, *Carbon* 44 (2006) 786–791.

Many efforts are currently focused on increasing densification while decreasing process time. The CVI gradient furnace proposed by Zhao et al. [13] is an example of a route to obtain a densified RL microstructure in a relatively short process time.

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Production processes for organic brake pads

4

4.1 Introduction: Types of processes

There are many types of processes used to effectively produce brake pads, but basically the following phases can be distinguished: mixing, molding, and curing (stabilization). The ways in which these phases are carried out are what characterize the process. The emphasis can be put on production rate, quality, costs, or stabilization of properties depending on the market in which the company is involved, whether original equipment, aftermarket, or the target end customers. This chapter does not deal with accessories or determining stages of the process such as the spring or wear detector applications, but only deals with the fundamental process steps that may affect the material performances. The main interconnected parameters are temperature, time, and pressure. High production rates may imply the use of high molding pressure and short times, displacing curing to the oven treatment. The processes related to lining and rolls are not considered, since they are already widely treated in other reports [1]. The most interesting developments concern disk brake pads. Batch and continuous processes are other discriminant aspects and faster processes are oriented towards continuous production. Since raw material price trends are towards a continuous increase, the innovations are directed to reducing costs by means of higher production rates and continuous in-line processes. The most interesting innovations in the last decades concern the use of unitary positive molds in rotatory presses that allow high control of process parameters and high production rates at the same time; the utilization of continuous ovens based either on convective or infrared (IR) heating; and electrostatic deposition of paints in IR ovens.

In summary, the production process of brake pads is evolving after many years of “starvation.” [Figure 4.1](#) illustrates the main changes that were faced in the last decade and are still going to be faced. All the main changes are directed towards making the process in-line faster and simpler as far as possible, moving from six steps to four.

The IR oven, based on direct natural gas (NG) flame heating a ceramic IR emitter, is a new type and represents a more efficient way to stabilize friction materials, since it increases the overall energy efficiency and decreases curing time for the contribution of the two types of heating: radiation and convection.

4.2 Blending

Blending is a delicate operation, often underestimated, but it is the initial stage of the pad production. Dry blending is currently the most common method; wet blending is going to be abandoned since it requires a solvent management system with significant

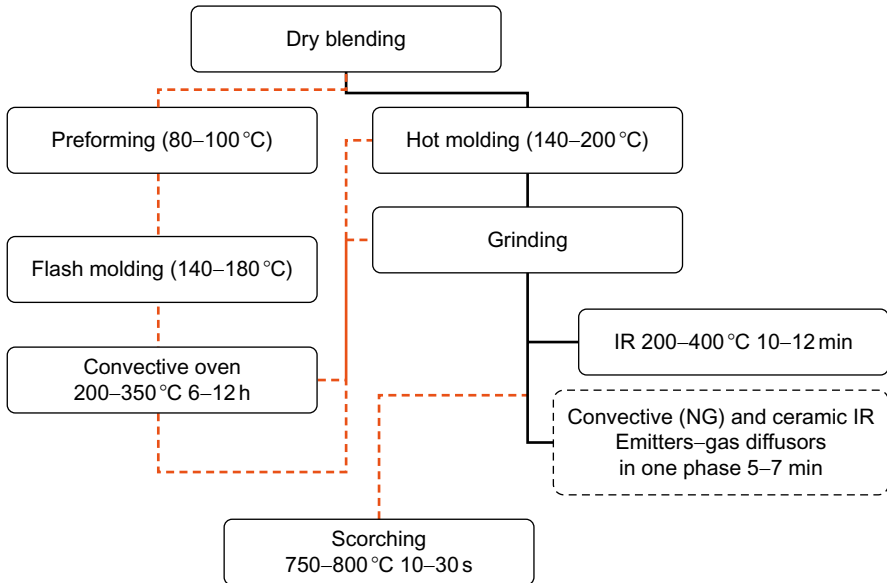


Figure 4.1 Flow diagram of both the old and updated production processes of brake pads. Continuous line: updated process; dotted line: old process.

environmental and safety issues. Blending is executed usually with blenders equipped with choppers and plow blades, in some cases also including nozzles to inject either gases or liquids. There are several empirical ideas on the blending order of the many components. The mixing operation is characterized by tribo-electrical charging and many of the advantages and disadvantages of dry mixing of powders are linked to this phenomenon, which can lead to an inappropriate mixing with segregation (not due to gravity as often thought).

Contact charging can be classified into three categories according to the contacting materials. There are metal–metal contact, metal–insulator contact, and insulator–insulator contact. Friction raw material powders are mainly both electrical insulators and metals. The most common contacts are metal–insulator and insulator–insulator. Most of the work on these phenomena is related to the pharmaceutical industry [2]. The models to describe the charging process of the insulator–insulator contact are similar to those of metal–insulator contacts, but the movement of electrons or ions in the insulating body is much more restricted. In the charging process of the metal–insulator category, three different paths can be distinguished. These are electron transfer, where the charging occurs by a flow of electrons; ion transfer, where ions are exchanged by diffusion and material transfer; and the path where material is rubbed off one contacting body and adheres on the other one.

Charge accumulation can occur only if at least one body is an insulator. The transferred contact charge is opposite and equal in the contacting bodies. The simple condenser model is a good approach to the complex phenomena of tribo-electrification. The model applied most often is that charge is exchanged when the contact is formed, in order to compensate the surface potential difference between the contacting bodies.

When separation occurs, the back-flow of the charge is hindered due to the poor surface conductivity of the contacting materials and therefore the charge remains on the contacting bodies. The arising of charge in powder mixing can be made the most of and utilized to improve mixture homogeneity or coating of large particles with small particles, since in friction materials' blends there are many different components that will be charged with opposite charges. In principle, it can be possible in dry mixing to prepare an ordered mixture, in which particles of one component adhere to the surface of another component. After a certain mixing time, the charge becomes constant and no improvements can be obtained, as shown for Aerosil in Figure 4.2 [2,3].

The factors that affect the extent and type of tribocharging are many and among them are the following: particle size and shape, surface roughness, nature and work function, contact material, impurities, relative humidity, and the energy of contact. Sliding or rubbing contact may reduce the surface work function and enforce the agility of the electrons, leading to an enhanced electron release [4].

The work function is the determining factor; in this regard, a semiquantitative tribo-electric series was proposed by Diaz and Felix-Navarro [5] in which a material with the up ranking will always be charged positively when in contact with a material lower down, because of the lower work function of materials of higher ranking. In contacts between metals and polymers, the polymers are charged positively when their highest occupied orbital is higher than the Fermi level. On the other hand, the polymer is charged negatively if the lowest unoccupied molecular orbital is lower than the Fermi level. The cases of contacts between insulators are more complex since there are no free electrons. However, to solve this problem a model has been built based on surface states, where the electrons are available to be transferred and driven by the difference between the work functions [6].

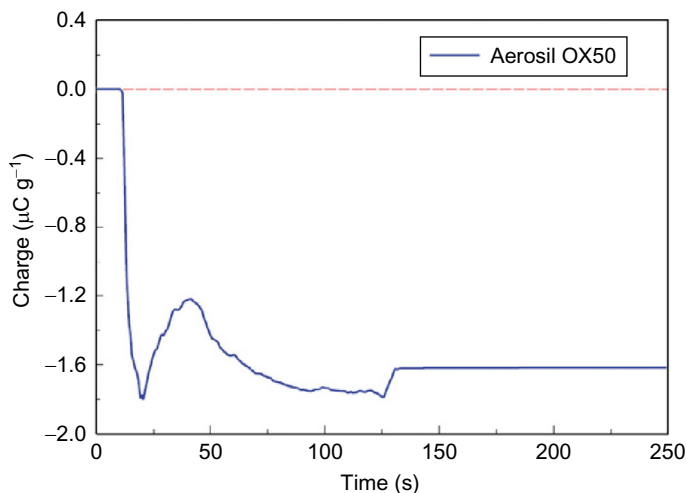


Figure 4.2 Electrostatic charge of Aerosil OX50 during dispersing [3].

S. Karner, N.A. Urbanetz, *The impact of electrostatic charge in pharmaceutical powders with specific focus on inhalation-powders*, *J. Aerosol Sci.* 42 (2011) 428–445.

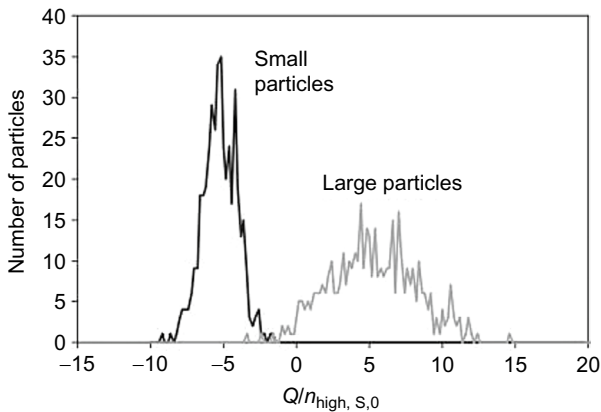


Figure 4.3 Distribution of charges on small and large particles at end of simulation. $n_{\text{high}, S, 0}$: initial population of high energy electrons for small particles.

D.J. Lacks, A. Levandovsky, Effect of particle size distribution on the polarity of triboelectric charging in granular insulator systems, J. Electrostat. 65 (2007) 107–112.

For example, as shown in Figure 4.3, large particles tend to charge positively, while small particles of the same insulator material charge negatively, as shown by Lacks and Levandovsky in a simulation based on the transfer of electrons of high energy to low energy states [7].

High levels of moisture decrease the charging amount, and charge dissipation is more favored by a longer rest time of the blend rather than the contact with the metallic walls of the blender, because most of the powders are insulators so that charges do not flow easily and not when in direct contact with walls.

These concepts of electrostatics are fundamental to developing adequate blending procedures. It is recommended not filling up the blender vessel to the top.

The most accepted concept is to divide blending into three or more phases. In the first one, most of the ceramic fillers with different enough size particles should be introduced, and air should be injected to favor a better mixing of fine particles and adhesion among particles than that provided by only the plows, since particles will then also be air suspended with better electrical charge and adhering among them. Organic fibril fibers such as aramid or polyacrylonitrile fibers must be introduced together with small amounts of metal powders, or preferably metal chips, both to favor electron exchange among particles and organic fibers and to break possible aggregates of ceramic powders, so that the interaction of fibers with ceramic particles is encouraged, while choppers are working to open fibrils. Finally, the other components are aggregated in order of crescent density, starting from graphite and carbon materials. In the last phase, most of the metals are added so that they do not usually stay more than 5 min in the mixer, preventing segregation. Mixing powders of different nature implies favoring adhesion among components, as well as seeking the right balance between an incomplete mixing with short mixing times and segregation with long mixing times (see Figure 4.4).

While the test methods to control the other phases of the process are well established and known, the methods to control the mixing effectiveness are still underdeveloped

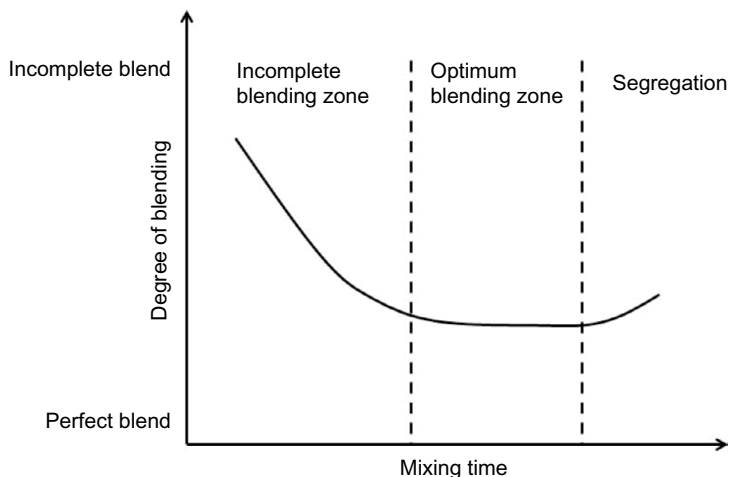


Figure 4.4 Qualitative diagram showing the degree of blending as a function of mixing time.

apart from apparent density. Granulometry cannot be adapted to blends because of the presence of fibers of different natures, which can considerably affect the reproducibility results. Methods based on chemical tracers and color tone are under study.

4.3 Positive molding

The use of positive molding is currently spreading, since more defined and uniform pressure on the blend during pressing is achievable with this method. With single positive mold, a more uniform temperature and pressure can be achieved. On the other hand, the so-called flash molding is on its way to being abandoned after many decades of being the dominant process, and is now used only by companies of low technology levels. The hot molding processes, which are designed to achieve the resin-curing temperature, usually work with temperatures between 150 and 200 °C and molding times between 10 and 3 min, depending upon the reactivity of the resin, the pad size, etc. Hot molding is essentially characterized by three phases. During the first stage, which is affected by the particle size and shape, densification processes occur, especially filling large voids. In the elastic–plastic stage, the densification is led by elastic deformation. Increasing pressure causes plastic deformation locally at particle contact points, depending upon their mechanical properties, and porosity dramatically decreases. Phenolic resin flow is increased by pressure, causing a further porosity decrease.

A sketch of a positive mold is shown in [Figure 4.5](#). It is possible to distinguish three parts: the die, the mold, and the plate. This concept can be extended to multiple molds, each one with its die. The heating of the three parts can be independent to create a gradient to favor heat flow through the pad.

A 600-ton press used for multiple positive molding is shown in [Figure 4.6](#). The force applied by the piston is then distributed to the dies. This solution is a compromise between the low-cost flash molding and the expensive rotating press with several single

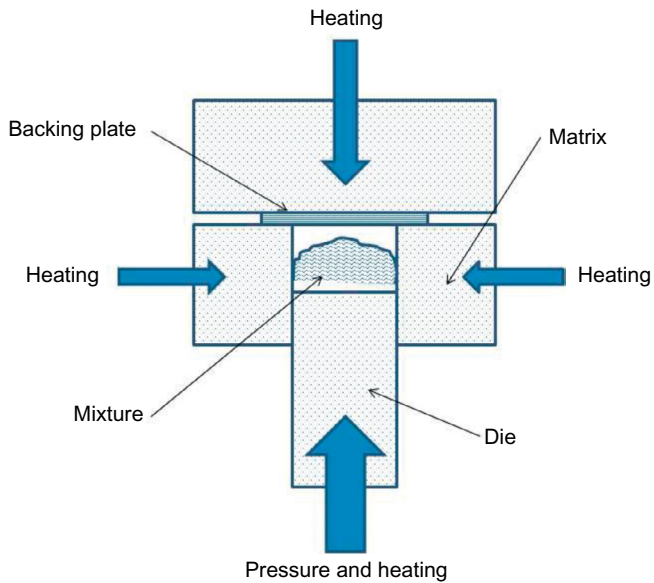


Figure 4.5 Sketch of a positive molding, depicting the high uniformity of pressure and heating achievable with this process.



Figure 4.6 600-ton press for multiple positive molding.
Courtesy of Isibond SaS, Italy.

positive molds. It should be noticed that flash molding needs a preliminary preforming step, while this phase can be avoided in positive molding as shown in [Figure 4.4](#).

With fast-curing resins, times of 2 min in medium size brake pads can be achieved, with areas around and below 100 cm². Although presses with multiple figure molds allow higher production rates, they do not exhibit uniform temperature and pressure in all the molds; there are always gradients which ultimately affect the quality of the products. A way to bypass this problem of high rate productivity with positive and unitary molding is to use rotary presses.

4.4 IR curing of friction materials

In updated processes, the IR in-line tunnel ovens are substituted for the batch convective oven with considerably improved time cycles: from 6–12 to 0.25 h—representing a true revolution in the field. These ovens are more effective because the radiation penetrates the material, heating the bulk as well, while in convective ovens the material heating by conduction is much slower. The wavelength range of ceramic heaters is usually between 2 and 10 μm . The heater temperature is usually between 500 and 700 °C. The temperatures on the pad surface may be above 300 °C, thus causing a scorching effect, which allows improvement of the friction performance of materials from the early stage of usage. The regulation of the belt speed may change the maximum temperature reached on the pad surface and bulk; also with the heater, the temperature may be changed to a certain extent. Moreover, these ovens often are equipped with mirrors to recover the scattered radiation. The metallic backing plate of the pad itself acts as a mirror reflecting the most radiation towards the bulk material. This procedure has overtaken the classic, additional scorching procedure that required pressing the friction surface with a hot plate at around 700 °C for 15–20 s.

The IR ovens are often characterized by different zones composed of several lamps or heaters with different temperatures. Usually the first zone has higher radiant temperature and a higher temperature rate increment, while the other two or three zones have the function of keeping the temperature constant for the remaining part of the treatment (see in this regard [Figure 4.7](#)).

The main objective of the curing process is not only to increase the resin cross-linking advancement in order to achieve low values of acetone, but also to carry out an accelerated aging to stabilize physical and mechanical properties, especially compressibility and starting pyrolysis of surface organics to quickly achieve a steady coefficient of friction during utilization.

4.5 Effect of production parameters on the material performances

The most important parameters are the molding temperature, pressure, and time. The curing temperature and duration have also a considerable effect. These parameters may affect the main characteristics of the brake pads: the coefficient of friction, such as

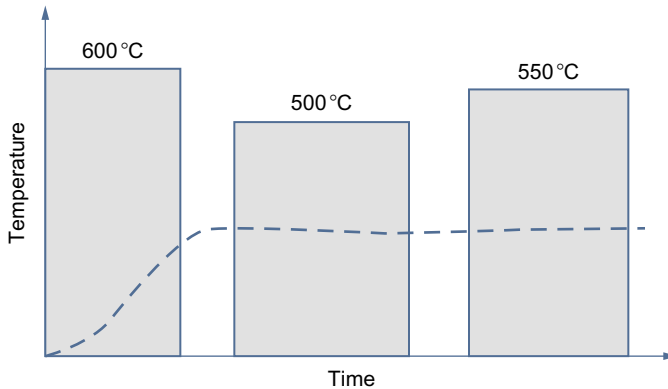


Figure 4.7 Temperatures of IR heaters (gray blocks) in a tunnel IR oven. The dotted line corresponds to the internal temperature of the pad. The treatment time to pass through the three zones is about 10–15 min.

bedding, recovery, wear rate in mild and severe conditions, compressibility as well as noise vibration and harshness NVH results. Molding temperature is related to the resin cross-linking and flow. Higher temperatures above 150°C increase reaction rate and reduce resin flow. Both high flow and high cross-linking are useful to the binding effects. Long molding times allow the cross-linking to advance further but this conflicts with high production rates. Moreover, higher pressure favors flow but increases byproduct gas pressure inside the mold, creating both external and internal cracks. The quick heat flow by conduction with higher temperature gradients from the mold surface towards the bulk may seal off the gases' exits, increasing the possibility of crack defects. It is noteworthy to point out that outgassing steps must be regulated to avoid molding cracks, and their number and duration depend upon the quantity and type of the resin used.

The sketch in [Figure 4.8](#) underlines the importance of searching out the right balance among several negative and positive properties. The negative properties, such as high wear rate, low resin flow which decreases material cohesion, and high porosity, can be minimized but never eliminated completely.

Large pads for commercial vehicles need longer times and higher temperature gradients (170–200°C on the mold matrix) than the smaller passenger car pads, because of the large volume/mass to be treated; also higher pressures are beneficial above 400 kg cm⁻². A new technique can be used to bypass some of the problems derived from the balance of molding parameters exposed in [Figure 4.9](#).

In spite of only using a pressure level during press molding, it is possible to use a double pressure. In the former stage a very low pressure is used, between 150 and 200 kg cm⁻², while in the second stage a pressure above 500 kg cm⁻² is achieved. This technique avoids the sealing effect of resin flow on the external pad surface, allowing the gases to flow during the high pressure stage, according to the sketch shown in [Figure 4.9](#).

The porosity is controlled and decreased by the compaction that is caused by the high pressure, but all the performances and properties of the friction materials are affected by the process.

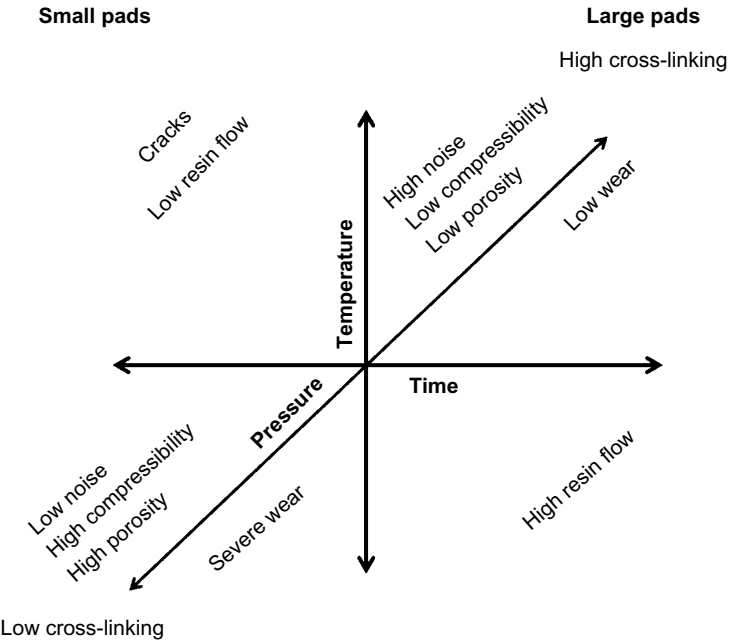


Figure 4.8 The effect of the molding parameters on the final properties and characteristics of the material. The right balance must be found. Sidelong properties depend strongly on pressure.

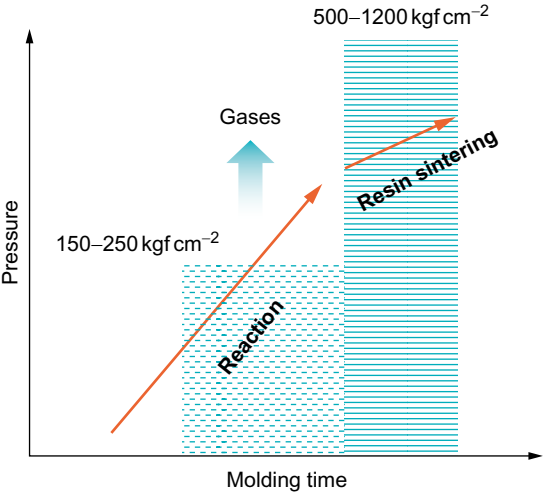


Figure 4.9 Double pressure system to mold commercial vehicle pads. In the first phase cross-linking advances allowing gases to flow.

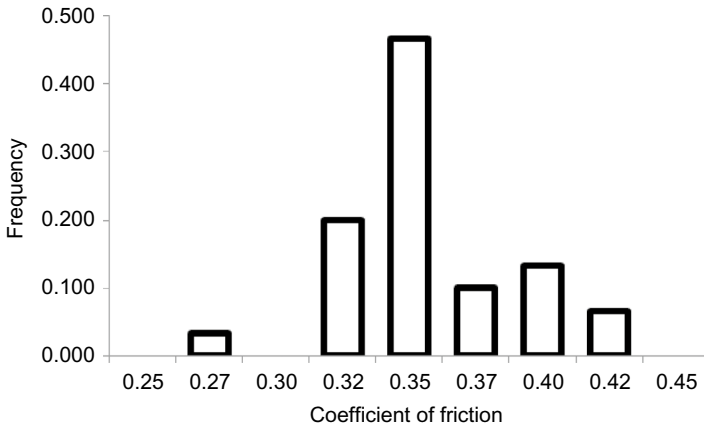


Figure 4.10 Cold coefficient of friction frequency as obtained in different batches of the same friction material.

In order to underline the relevance of the process in defining the final properties of the material and the control of process parameters, a frequency histogram of the coefficient of friction is shown in [Figure 4.10](#) for 30 samples of a specific friction material block part produced using the same formula. The values used for the distribution shown are the so-called “cold coefficients of friction” in the standard J661 [8]. This test was carried out for 30 different samples, each one coming from different batches, taken at the end of the process ready to be delivered. It is possible to distinguish three very different groups of materials, characterized by coefficients of friction centered at 0.27, 0.35, and 0.40, respectively.

A study conducted by Ertan and Yavuz [9] reports the effect of the intentional variation of certain process parameters on a non asbestos organic NAO material performance, and they found that both the coefficient of friction and wear are strongly affected even by variations around 10% of the considered parameter in the case of molding temperature, and about 20% in the case of molding pressure. In conclusion, the variability of the material properties depends to a large extent on the production process, with temperature and pressure being without a doubt the most important parameters.

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6.1 Introduction

Metal sulfides are not simple fillers (if the term can be used) but fundamental components of friction materials. They give an added value necessary when performances are very demanding. They stabilize the coefficient of friction, reducing the sensitivity to both speed and pressure. Their effect also is in relation to their capacity to be transformed into oxide in the air atmosphere and deposited on the rotor surface, altering the chemical–physical and tribological properties. Metal sulfides are the subject of tribochemical reactions, i.e., specially activated by friction in conditions different from purely thermally activated reactions. The structure of the different types of sulfides is very variable, passing from lamellar structures (such as those exhibited by the orthorhombic structure) with weak interplanar interactions, to three-dimensional (3D) stronger and harder frameworks, such as zinc blende structures. There are two aspects to be considered for metal sulfides in relation to their relevance in friction materials: their structure and their reactivity to form oxides.

Structure is related to the ability to lubricate and the oxide formation is related to the change from a soft material to a harder one. The true sulfide lubricant is the famous MoS_2 , which forms layers with an interplanar distance of 3.49 Å and can lubricate until it is transformed to MoO_3 in air above 500 °C. The sliding properties of MoS_2 are due to the weak interactions between the sulfur atoms of adjacent layers (see the layers in [Figure 6.1](#)). In the MoS_2 structure, each Mo(IV) center occupies a trigonal prismatic coordination sphere, being bound to six sulfide ligands.

Another aspect to be considered is the tendency of sulfur to form polymer chains and sulfur–sulfur bonds; this makes the types of structures (polymorphism) that can be possible and present very complex, even for the same stoichiometric compound.

However, the most emblematic sulfide is diantimony trisulfide Sb_2S_3 , which improves fade resistance by developing transfer films on the disk surface at elevated temperatures. The friction materials containing Sb_2S_3 exhibit a lower stick-slip propensity than those friction materials with graphite [1]. The improved fade resistance with Sb_2S_3 is usually attributed to its lubricating capability sustained at high temperatures, while the lower stick-slip propensity of the friction materials with Sb_2S_3 is associated with the slight difference between its static and kinetic coefficients of friction and high normal stiffness. In the last few years tin sulfides are being substituted in many friction applications for their marked lubricating characteristics coupled with tribochemical reactions to form oxides. The mechanism of tribochemical reactions is under discussion because the theory which is considered implies that exoelectrons produced by friction work can deliver energy to an activated transition state. Most sulfides are semiconductors and friction can easily activate electrons and promote the formation of oxides.

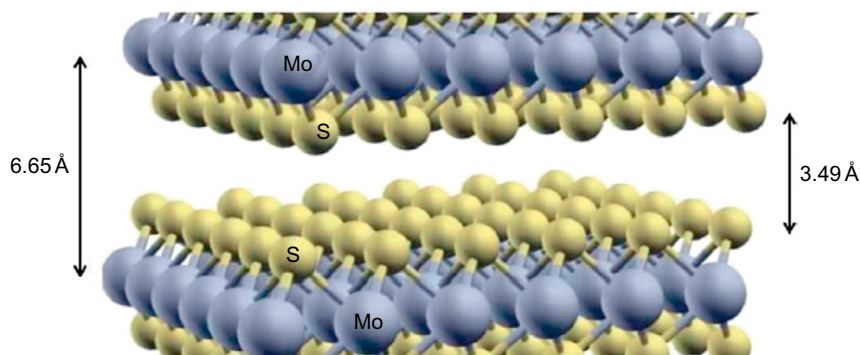


Figure 6.1 View of MoS₂ layers.

6.2 Tin sulfide

Due to the versatile characteristics of coordination of both tin and sulfur, tin sulfides may have several structures. As a member of the 4A group in the fifth row of the periodic table, Sn can have coordination numbers from 2 to 9 so that many geometrical arrangements are possible. The most common ones are trigonal-pyramidal coordination for Sn(II), while tetrahedral, trigonal bipyramidal, and octahedral coordinations are common for Sn(IV). Sulfur, which belongs to the 6A group and third row, exhibits many coordination arrangements. In addition, sulfur has the ability to form chains of variable length. This property led to the synthesis of many types of sulfides: 1D, 2D, and 3D frameworks.

New methods of synthesis of SnS, starting from SnCl₂ and elemental sulfur dissolved in oleylamine, have demonstrated the possibility of tuning the formation of SnS with zinc blende structures and orthorhombics by changing the synthesis temperature from 170 to 230 °C [2] with yields above 90%. The orthorhombic phase is a 2D material that fits adequately into friction applications. The platelets obtained are shown in a SEM image in Figure 6.2.

The tetrahedral geometry is often present for Sn(IV) thiostannate polymers; however, more synthetic compounds are appearing with this geometry. Sn₂S₃, also known as the mineral ottemanite, is a mixed valence sulfide with Sn(II) and Sn(IV) with a ribbon structure and can be prepared by heating a stoichiometric quantity of sulfur and elemental tin powders at 720 °C.

The Sn(IV) sites are octahedrally coordinated in the ribbon, while the Sn(II) sites occupy trigonal-pyramidal sites. This compound exhibits polymorphism and at least three different types have been identified: α-Sn₂S₃, β-Sn₂S₃, and γ-Sn₂S₃ [3]. The main structure of this compound is shown in Figure 6.3. It is noteworthy to point out that Sn(II) is on the edge while Sn(IV) is in the middle.

The α and β phases are nonstoichiometric, being Sn_{2±x}S₃, and are stable above 700 °C, while the γ phase is stable below 675 °C. In general tin sulfide favors a 2D structure either flat or undulated. The typology of the layers' structures varies from a close packing to more open structures with variable geometries. The layered structure of tin sulfide favors the typical characteristic of a lubricant or lubricant coadjutant.

2 μm

20 nm

Figure 6.2 SEM images of 2D orthorhombic plates of SnS after a reaction time of 10 min. The plates are terminated by (010) and (001) or (011) edges (inset: micrometer-sized plates synthesized after a reaction time of 3 h).

E.C. Greyson, J.E. Barton, T.W. Odom, Tetrahedral zinc blende tin sulfide nano and microcrystals, Small 2 (2006) 368–371.

Tin monosulfide, SnS, known as the mineral herzenbergite, can be prepared by stoichiometric quantities of S and Sn at temperatures between 600 and 750 °C. The structure is composed of layers with a distance of 3.383 Å. Sn is coordinated in a very distorted octahedron with three short bonds of 2.7 Å and three long ones nearly 3.4 Å with S. The layered structure is shown in [Figure 6.4](#).

Tin disulfide, SnS₂, is synthesized through the technique of chemical vapor transport (CVT) at temperatures between 650 and 950 °C using I₂ as transport agent. This method implies that Sn and S are mixed in stoichiometrically but the first reaction involves Sn and I₂:

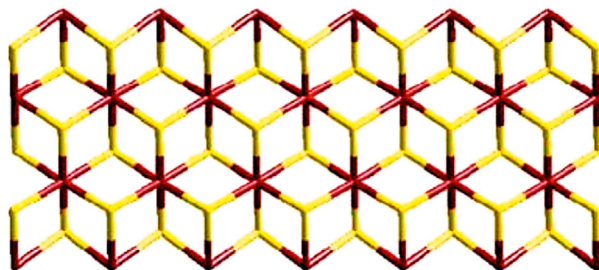


Figure 6.3 A representation of the ribbon structure of Sn₂S₃, the trigonal-pyramidal Sn(II) locating at the edge and the octahedral Sn(IV) at the center of the ribbon with six coordinated sulfur atoms [2].

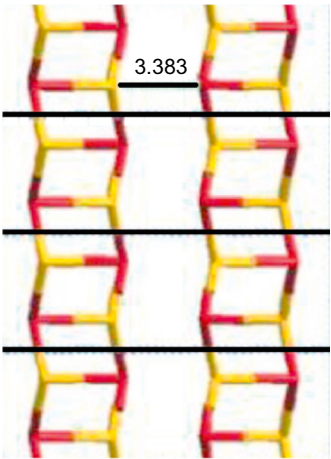


Figure 6.4 A double layer of SnS. Dark atoms: Sn, clear atoms: S.

The tin iodide passes to the gas and further reacts with sulfur to form the final product SnS₂:



The two reactions occur to opposite sides of a tubular reactor with a temperature gradient applied with a temperature T_1 greater than the temperature T_2 where the tin sulfide is deposited.

The CVT process is very common and the atomic ratio is very important to determine the phases of sulfides obtained. Table 6.1 resumes the different phases obtained by CVT with the corresponding T_1 and T_2 temperatures [4].

Tin disulfide adopts the PbI₂ layered structure with a hexagonal unit cell, in which tin atoms are located in the octahedral sites between two hexagonally

Table 6.1 Phases detected by X-ray diffraction analysis

Atomic ratio (Sn:S)	Temperature (°C)		
	950–850	850–750	750–650
1:1	SnS	SnS + Sn ₂ S ₃	Sn ₂ S ₃ + SnS
2:3	Sn ₂ S ₃ + SnS (traces)	SnS + Sn ₂ S ₃ + SnS ₂	Sn ₂ S ₃ + SnS
3:4	Sn ₂ S ₃ + SnS	SnS + Sn ₂ S ₃ + SnS ₂	Sn ₂ S ₃ + SnS
4:5	Sn ₂ S ₃ + SnS	SnS + Sn ₂ S ₃	Sn ₂ S ₃ + SnS (traces)
1:2	SnS ₂	SnS ₂	SnS ₂

M. Cruz, J. Morales, J.P. Espinos, J. Sanz, XRD, XPS and 119Sn NMR study of tin sulfides obtained by using chemical vapor transport methods, J. Solid State Chem. 175 (2003) 359–365.

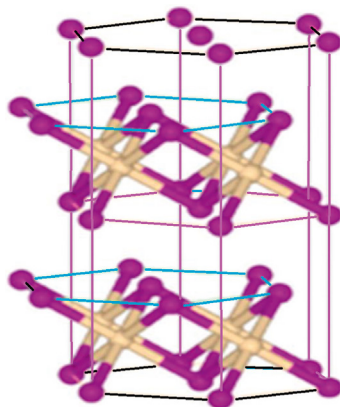


Figure 6.5 SnS_2 structure with appreciable hexagonal packing of sulfur.

close-packed sulfur slabs to form a sandwich structure, as shown in [Figure 6.5](#). The SnS_2 layer can be viewed as composed of all-edge-sharing octahedral SnS_6 building units with the sulfurs exhibiting three-coordination and local trigonal-pyramidal symmetry. The SnS_2 layers are then stacked on top of one other along the crystallographic c -axis and held together by weak van der Waals forces. There are many ways to stack these layers together to create various polytypes. More than 70 polytype structures of SnS_2 have been established through a complicated single crystal structure analysis procedure. All of the polytypes have the same hexagonal close-packed structure within the layer and with an identical cell parameter a of $3.647 \text{ \AA}$, and interplanar distance of $5.889 \text{ \AA}$. However, the c parameter can vary and be very large because of the variable offset between layers that gives origin to many polytypes.

In some cases, the unit cell size in the c direction may reach more than $700 \text{ \AA}$! Moreover, in the same crystal several phases of polytypes may coexist. Palosz et al. [5] suggested that this stacking variety is due to the partial occupancy of the site by Sn and S in the lattice, and that it is a consequence of the versatile bonding nature of tin and sulfur, which gives rise to many stoichiometric and nonstoichiometric compounds as well as lattice-site deficient structures.

6.3 Triboxidation of metal sulfides

The tribological characteristics that make metal sulfides different from graphite are at least three:

- i. Metal sulfides' lubrication is not affected to the same extent by impurities such as humidity and air that make graphite more lubricating, but at higher temperatures when water is removed the lubricant effect decreases. This is due to the fact that, in the graphite case, water reduces the covalent bond degree between adjacent layers.

- ii. Metal sulfides are thermally oxidized in a temperature range of 300–600 °C. The oxides formed are usually harder than the corresponding sulfides providing a behavior transition with a consequent increasing of the coefficient of friction. This can counterbalance the loss of friction due to carbon-based lubricants. In addition, in many sulfides the substitution of sulfur with oxygen implies a change of the oxidation state of the metal element. For example, Mo(IV) sulfide easily forms Mo(VI) oxide. This change inevitably causes a considerable structure alteration, also when lamellar structure is preserved. On the other hand, the main (and final) product of graphite oxidation (the carbon-based solid lubricant) is the gaseous CO₂ which is released without any contribution to friction and causes a massive wear loss. Moreover, the sudden emissions of CO₂ can decrease friction between the sliding surfaces.
- iii. It is well known that the oxidation can be activated by friction through the negative ion-radical action mechanism (NIRAM) with considerably higher rates than the thermally activated reactions [6], thus making these reactions very sensitive to change of brake pressure and rotor speed, which creates a feed-in energy to speed up these chemical reactions. Indeed, the semiconductor nature of most sulfides can provide low energy electrons excited by friction work. These electrons intervene in the transition state formation by lowering the activation energy.

The whole reaction in the case of MoS₂ is the following:



According to NIRAM, electrons are released by friction work and can react to form an oxygen radical ion which attacks the sulfide framework. Dangling bonds also are formed and many radicals are present on the surface, apart from those described in Figure 6.6. Humidity also plays a role as an alternative to oxygen. The mechanism described by means of NIRAM theory involves the formation of a triboplasma.

The case of MoS₂ oxidation adequately illustrates the changes of structure. The orthorhombic and monoclinic phases of Mo(VI) oxides are called α-MoO₃ and β-MoO₃, respectively.

The orthorhombic phase is the most stable and probably is that formed during friction in air. α-MoO₃ is a lamellar solid and consists of a double layer of distorted MoO₆ octahedra. The adjacent layers are linked by weak van der Waals forces. The cell parameters are $a = 13.86 \text{ \AA}$, $b = 3.70 \text{ \AA}$, $c = 3.96 \text{ \AA}$ [7] and the layered structure of

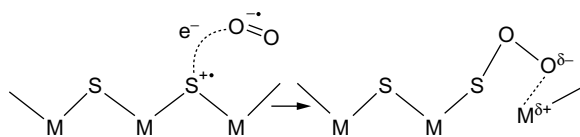


Figure 6.6 Possible mechanism of a metal sulfide oxidation in air under dry friction. The transition state (on the right) is the same as for the thermally activated reaction.

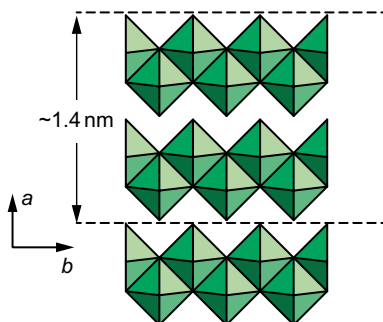


Figure 6.7 View of the α - MoO_3 structure along the a and b directions.

K. Kalantar-zadeh, K. Galatsis, J. Tang, R. Kojima, M. Wang, V. Strong, K.L. Wang, A. Lech, A. Shailos, W. Wlodarski, R.B. Kaner, Synthesis of nanometre-thick MoO_3 sheets, Nanoscale 2 (2010) 429–433.

zigzagged sheets made of MoO_6 octahedra is shown in Figure 6.7. The thickness of the double layer including a van der Waals gap is $13.86 \text{ \AA}$ ($\sim 1.4 \text{ nm}$). The interlayer gap is about $2 \text{ \AA}$, i.e., considerably lower than the $3.49 \text{ \AA}$ of MoS_2 , which will cause a less lubricating effect of the Mo(VI) oxide in comparison to the Mo(IV) sulfide.

6.4 Sb_2S_3 : A paradigm for all metal sulfides in brake applications

Antimony trisulfide is currently the most effective metal sulfide in the friction industry. This fact demonstrates that not only the lubricant effect is desired, but also the oxide formation and change of oxidation state of the metal element is a determining factor.

Sb_2S_3 crystallizes in the orthorhombic system. Each Sb atom is bound to three oxygen atoms forming a trigonal pyramid according to Figure 6.8. The cell parameters are the following: $a = 11.223 \text{ \AA}$, $b = 11.311 \text{ \AA}$, $c = 3.839 \text{ \AA}$ [8,9]. Some authors exchange the cell parameters although the values are quite similar. Moreover, the cell parameters vary with temperature passing from monoclinic below 20°C to orthorhombic. The material consists of ribbons of Sb_2S_3 (four for each cell) parallel to the c direction, which form chains of ribbon pairs Sb_4S_6 . The Sb and S of neighbors have distances in the range of 3.11 – $3.64 \text{ \AA}$. Each pair is weakly linked to the neighbor chain. This characteristic of forming weakly linked chains is what provides the lubricant properties.

The tribooxidation products can be antimony oxides containing both Sb(III) and Sb(V) . The main product Sb_2O_3 has an orthorhombic structure and forms $-\text{O}-\text{Sb}-\text{O}-\text{Sb}-\text{O}-$ chains that are linked through terminal oxygen atoms.

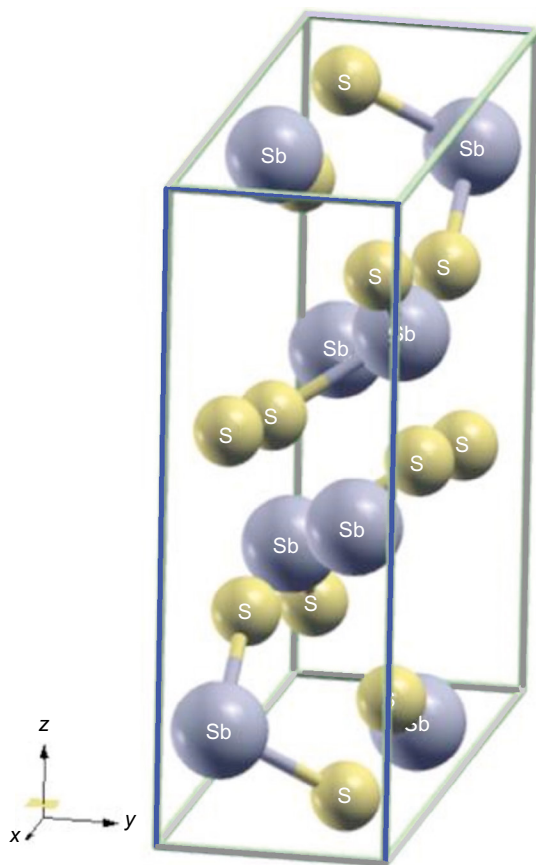


Figure 6.8 Crystal structure of Sb_2S_3 .

T. BenNasr, H. Maghraoui-Meherzi, H. BenAbdallah, R. Bennaceur, Electronic structure and optical properties of Sb_2S_3 crystal, Physica B 406 (2011) 287–292.

6.5 Synergy between sulfides and abrasives

The synergy between abrasives and sulfides is very interesting. In this regard, a study by Jang and Kim [10] on non asbestos organic NAO formulas showed that the best balance between ZrSiO_4 and Sb_2S_3 is with the ratio 1:1; in the specific case, the percent of the two variable components was 4 vol%. The coefficient of friction obtained is relatively stable and high enough with this ratio, with a maximum around 0.38 at 250 °C in a full-scale drag test [10].

This research report highlighted another relevant indirect effect of Sb_2S_3 , which is that of disk thickness variation (DTV). The blends with a higher content of Sb_2S_3 (up to 6 vol%) exhibited a lower brake torque variation (fewer vibrations) due to a lower DTV, since large amounts of the abrasive zirconium silicate causes a higher instability mainly due to the high coefficient of friction (see Chapter 5). The lowest wear was

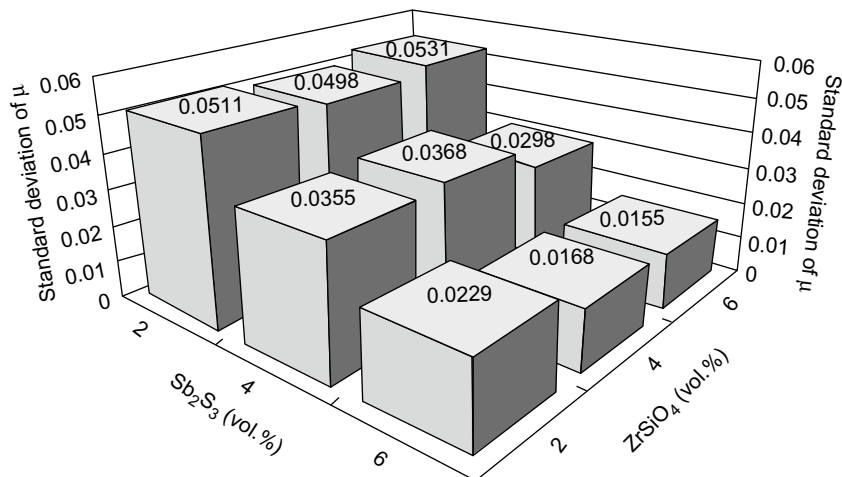


Figure 6.9 Stability of friction coefficient, represented as standard deviation of different μ values from 20 different stop conditions.

H. Jang, S.J. Kim, *The effects of antimony trisulfide Sb₂S₃ and zirconium silicate ZrSiO₄ in the automotive brake friction material on friction characteristics*, *Wear* 239 (2000) 229–236.

also obtained with the highest content of Sb₂S₃ at 6 vol% and the lowest one of ZrSiO₄. However, the most outstanding effect of Sb₂S₃ is the stabilization of the friction level, and in this case synergy can be found between sulfides and abrasives as in the case mentioned with ZrSiO₄.

Figure 6.9 exposes this effect quite clearly by reporting the standard deviation of the coefficient of friction during stop in different conditions. The lowest standard deviation was found again for the ratio 1:1 but with 6 vol% of both components. However, the effect of Sb₂S₃ on stabilization of the coefficient of friction is very marked, while that of ZrSiO₄ is much less and seems to be due to a sort of “cooperation” between the two materials.

This result suggests that Sb₂S₃ in the friction material plays an important role in improving friction stability [10].

The synergy between the abrasive and the sulfide can be understood in terms of surface modifications induced by the sulfide upon abrasive action. The mechanism can be depicted as follows: abrasives remove the oxide layer, exposing the metal surface, and then the sulfides are easily deposited due to their either lamellar or chain structure. At this point the sulfides are oxidized, and the oxides, less adhesive than sulfides, are removed again by abrasives or delamination after a limit thickness has been reached. In this way a protective action of the metallic surface is provided. Through this mechanism thermal DTV and cracks by thermal–mechanical fatigue are prevented (e.g., in commercial vehicles).

The stabilization of the coefficient of friction is obtained through a balance between adhesion and deformation forces that decrease the effect of variables such as speed and pressure, according to Equation (2.23):

$$\mu = \frac{\beta p + \tau}{p} = \beta + \frac{\tau}{p} \quad (6.4)$$

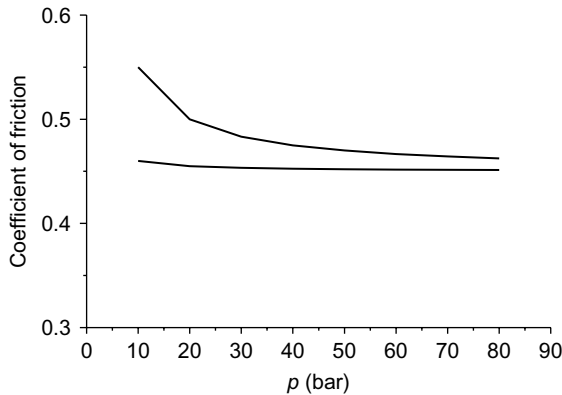


Figure 6.10 An example of sensitivity to pressure. In the upper curve τ was 0.1 bar and in the lower one 1 bar, while β was in both cases 0.45.

where both β and τ are terms linked to adhesion forces; however, β is correlated to the enlargement of adhesion due to deformation, and p is pressure. This equation expresses the sensitivity of the coefficient of friction to pressure. If the component that expresses the shear strength τ of the film of sulfide–oxide composite is low, the sensitivity to pressure would be less marked, because the steady value will be reached quickly. The term τ seems to depend mostly on the sulfides. The value of β will depend also on sulfides and the sliding surfaces' contact. This is a clear example of the balance between opposites that is sought to achieve adequate friction material performances. Figure 6.10 shows an example of sensitivity to pressure according to Equation (6.4).

It is interesting to notice the evolution of ratios among the components of a formula towards a lower sensitivity to both pressure and speed in a hybrid formula. The greatest benefit for the specific formula was found for ratios of sulfides:abrasives:metals of 0.42:0.17:0.41 as shown in the ternary diagram of Figure 6.11.

The speed sensitivity as function of the ratio between sulfides and metals for the formula development mentioned is reported in Figure 6.12 for a full dyno performance test. This graphic clearly shows that metal sulfides are more determinant than metals. However, a certain degree of cooperation and a compromise between the two main contributors to the tribofilm on the disk surface is reached. In fact, according to Figure 6.12, below a certain ratio of metals even the sulfide effect is faded.

Metal sulfides basically transfer metals from the friction material to the disk surface, acting as a lubricating soft and lamellar solid that favors the deposition and formation of a steady composite metallic tribofilm on the rotor surface, and it seems they do better than solid metals.

Evidence of the transfer film of Sb has been reported in many studies, and the low content of S found confirms the idea that a composite oxide layer is formed containing FeOx and even very small graphite/carbon particles [11]. The thermal properties of metal sulfide connected to their ability to be oxidized seem to be the determiners

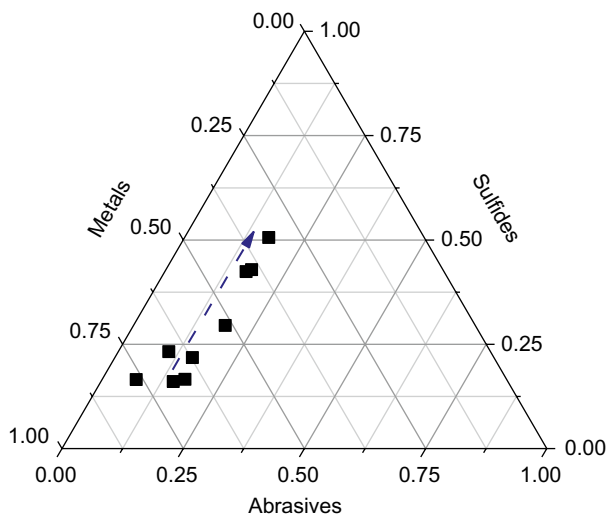


Figure 6.11 Ternary diagram showing the path of a formula optimization towards the sulfides' increasing (see the arrow).

of this effect. The differential scanning calorimetry of Sb_2S_3 (Figure 6.13) shows that there are two main transformations: the former around 300°C attributable to the exchange reaction between S and O to form Sb_2O_3 , the latter at 550°C to the oxidation of Sb(III) to Sb(V) to form Sb_2O_5 . These reactions when activated by friction can be faster and occur at lower temperatures. The thermal and tribochemical characteristics of metal sulfides make them the keystone of friction materials.

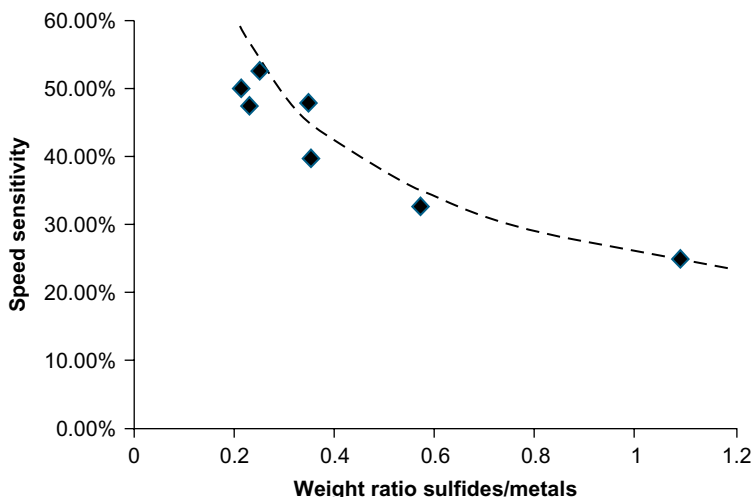


Figure 6.12 Speed sensitivity as function of the ratio between metal sulfides and metals.

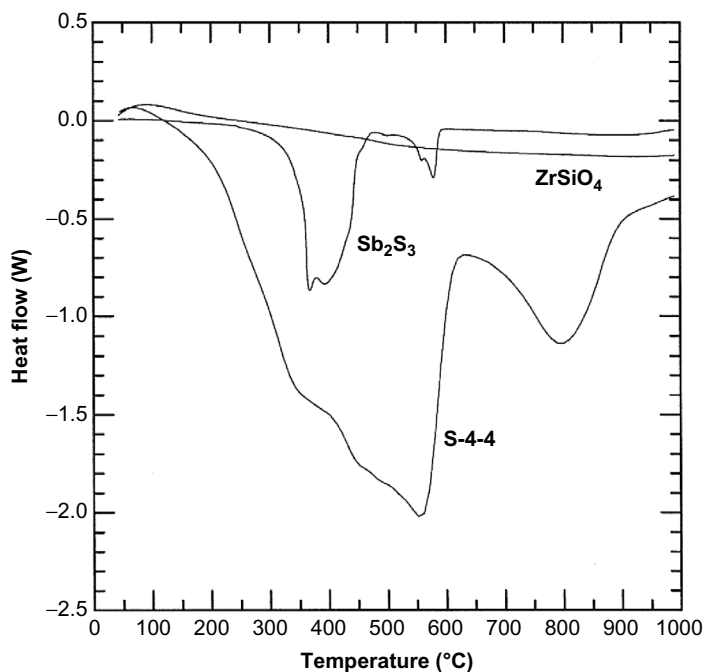


Figure 6.13 Differential scanning calorimetry curves for Sb_2S_3 , zircon silicate, and a NAO friction material containing both raw materials.

H. Jang, S.J. Kim, *The effects of antimony trisulfide Sb_2S_3 and zirconium silicate ZrSiO_4 in the automotive brake friction material on friction characteristics*, *Wear* 239 (2000) 229–236.

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- [8] T. BenNasr, H. Maghraoui-Meherzi, H. BenAbdallah, R. Bennaceur, Electronic structure and optical properties of Sb_2S_3 crystal, *Physica B* 406 (2011) 287–292.
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6.1 Introduction

Metal sulfides are not simple fillers (if the term can be used) but fundamental components of friction materials. They give an added value necessary when performances are very demanding. They stabilize the coefficient of friction, reducing the sensitivity to both speed and pressure. Their effect also is in relation to their capacity to be transformed into oxide in the air atmosphere and deposited on the rotor surface, altering the chemical–physical and tribological properties. Metal sulfides are the subject of tribochemical reactions, i.e., specially activated by friction in conditions different from purely thermally activated reactions. The structure of the different types of sulfides is very variable, passing from lamellar structures (such as those exhibited by the orthorhombic structure) with weak interplanar interactions, to three-dimensional (3D) stronger and harder frameworks, such as zinc blende structures. There are two aspects to be considered for metal sulfides in relation to their relevance in friction materials: their structure and their reactivity to form oxides.

Structure is related to the ability to lubricate and the oxide formation is related to the change from a soft material to a harder one. The true sulfide lubricant is the famous MoS_2 , which forms layers with an interplanar distance of 3.49 Å and can lubricate until it is transformed to MoO_3 in air above 500 °C. The sliding properties of MoS_2 are due to the weak interactions between the sulfur atoms of adjacent layers (see the layers in [Figure 6.1](#)). In the MoS_2 structure, each Mo(IV) center occupies a trigonal prismatic coordination sphere, being bound to six sulfide ligands.

Another aspect to be considered is the tendency of sulfur to form polymer chains and sulfur–sulfur bonds; this makes the types of structures (polymorphism) that can be possible and present very complex, even for the same stoichiometric compound.

However, the most emblematic sulfide is diantimony trisulfide Sb_2S_3 , which improves fade resistance by developing transfer films on the disk surface at elevated temperatures. The friction materials containing Sb_2S_3 exhibit a lower stick-slip propensity than those friction materials with graphite [1]. The improved fade resistance with Sb_2S_3 is usually attributed to its lubricating capability sustained at high temperatures, while the lower stick-slip propensity of the friction materials with Sb_2S_3 is associated with the slight difference between its static and kinetic coefficients of friction and high normal stiffness. In the last few years tin sulfides are being substituted in many friction applications for their marked lubricating characteristics coupled with tribochemical reactions to form oxides. The mechanism of tribochemical reactions is under discussion because the theory which is considered implies that exoelectrons produced by friction work can deliver energy to an activated transition state. Most sulfides are semiconductors and friction can easily activate electrons and promote the formation of oxides.

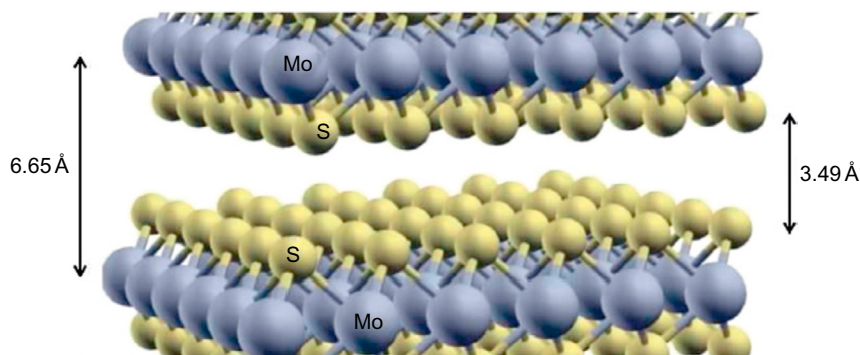


Figure 6.1 View of MoS₂ layers.

6.2 Tin sulfide

Due to the versatile characteristics of coordination of both tin and sulfur, tin sulfides may have several structures. As a member of the 4A group in the fifth row of the periodic table, Sn can have coordination numbers from 2 to 9 so that many geometrical arrangements are possible. The most common ones are trigonal-pyramidal coordination for Sn(II), while tetrahedral, trigonal bipyramidal, and octahedral coordinations are common for Sn(IV). Sulfur, which belongs to the 6A group and third row, exhibits many coordination arrangements. In addition, sulfur has the ability to form chains of variable length. This property led to the synthesis of many types of sulfides: 1D, 2D, and 3D frameworks.

New methods of synthesis of SnS, starting from SnCl₂ and elemental sulfur dissolved in oleylamine, have demonstrated the possibility of tuning the formation of SnS with zinc blende structures and orthorhombics by changing the synthesis temperature from 170 to 230 °C [2] with yields above 90%. The orthorhombic phase is a 2D material that fits adequately into friction applications. The platelets obtained are shown in a SEM image in Figure 6.2.

The tetrahedral geometry is often present for Sn(IV) thiostannate polymers; however, more synthetic compounds are appearing with this geometry. Sn₂S₃, also known as the mineral ottemanite, is a mixed valence sulfide with Sn(II) and Sn(IV) with a ribbon structure and can be prepared by heating a stoichiometric quantity of sulfur and elemental tin powders at 720 °C.

The Sn(IV) sites are octahedrally coordinated in the ribbon, while the Sn(II) sites occupy trigonal-pyramidal sites. This compound exhibits polymorphism and at least three different types have been identified: α-Sn₂S₃, β-Sn₂S₃, and γ-Sn₂S₃ [3]. The main structure of this compound is shown in Figure 6.3. It is noteworthy to point out that Sn(II) is on the edge while Sn(IV) is in the middle.

The α and β phases are nonstoichiometric, being Sn_{2±x}S₃, and are stable above 700 °C, while the γ phase is stable below 675 °C. In general tin sulfide favors a 2D structure either flat or undulated. The typology of the layers' structures varies from a close packing to more open structures with variable geometries. The layered structure of tin sulfide favors the typical characteristic of a lubricant or lubricant coadjutant.

2 μm

20 nm

Figure 6.2 SEM images of 2D orthorhombic plates of SnS after a reaction time of 10 min. The plates are terminated by (010) and (001) or (011) edges (inset: micrometer-sized plates synthesized after a reaction time of 3 h).

E.C. Greyson, J.E. Barton, T.W. Odom, Tetrahedral zinc blende tin sulfide nano and microcrystals, Small 2 (2006) 368–371.

Tin monosulfide, SnS, known as the mineral herzenbergite, can be prepared by stoichiometric quantities of S and Sn at temperatures between 600 and 750 °C. The structure is composed of layers with a distance of 3.383 Å. Sn is coordinated in a very distorted octahedron with three short bonds of 2.7 Å and three long ones nearly 3.4 Å with S. The layered structure is shown in [Figure 6.4](#).

Tin disulfide, SnS₂, is synthesized through the technique of chemical vapor transport (CVT) at temperatures between 650 and 950 °C using I₂ as transport agent. This method implies that Sn and S are mixed in stoichiometrically but the first reaction involves Sn and I₂:

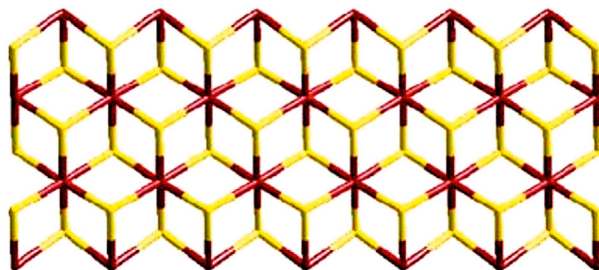


Figure 6.3 A representation of the ribbon structure of Sn₂S₃, the trigonal-pyramidal Sn(II) locating at the edge and the octahedral Sn(IV) at the center of the ribbon with six coordinated sulfur atoms [2].

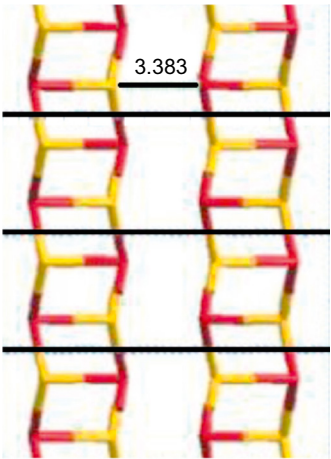


Figure 6.4 A double layer of SnS. Dark atoms: Sn, clear atoms: S.

The tin iodide passes to the gas and further reacts with sulfur to form the final product SnS₂:



The two reactions occur to opposite sides of a tubular reactor with a temperature gradient applied with a temperature T_1 greater than the temperature T_2 where the tin sulfide is deposited.

The CVT process is very common and the atomic ratio is very important to determine the phases of sulfides obtained. Table 6.1 resumes the different phases obtained by CVT with the corresponding T_1 and T_2 temperatures [4].

Tin disulfide adopts the PbI₂ layered structure with a hexagonal unit cell, in which tin atoms are located in the octahedral sites between two hexagonally

Table 6.1 Phases detected by X-ray diffraction analysis

Atomic ratio (Sn:S)	Temperature (°C)		
	950–850	850–750	750–650
1:1	SnS	SnS + Sn ₂ S ₃	Sn ₂ S ₃ + SnS
2:3	Sn ₂ S ₃ + SnS (traces)	SnS + Sn ₂ S ₃ + SnS ₂	Sn ₂ S ₃ + SnS
3:4	Sn ₂ S ₃ + SnS	SnS + Sn ₂ S ₃ + SnS ₂	Sn ₂ S ₃ + SnS
4:5	Sn ₂ S ₃ + SnS	SnS + Sn ₂ S ₃	Sn ₂ S ₃ + SnS (traces)
1:2	SnS ₂	SnS ₂	SnS ₂

M. Cruz, J. Morales, J.P. Espinos, J. Sanz, XRD, XPS and 119Sn NMR study of tin sulfides obtained by using chemical vapor transport methods, J. Solid State Chem. 175 (2003) 359–365.

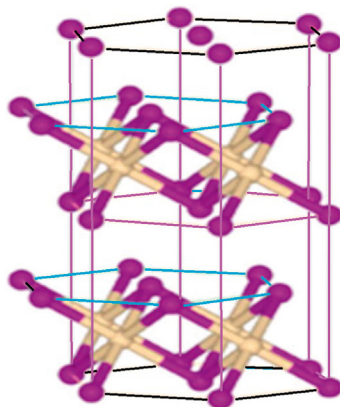


Figure 6.5 SnS_2 structure with appreciable hexagonal packing of sulfur.

close-packed sulfur slabs to form a sandwich structure, as shown in [Figure 6.5](#). The SnS_2 layer can be viewed as composed of all-edge-sharing octahedral SnS_6 building units with the sulfurs exhibiting three-coordination and local trigonal-pyramidal symmetry. The SnS_2 layers are then stacked on top of one other along the crystallographic c -axis and held together by weak van der Waals forces. There are many ways to stack these layers together to create various polytypes. More than 70 polytype structures of SnS_2 have been established through a complicated single crystal structure analysis procedure. All of the polytypes have the same hexagonal close-packed structure within the layer and with an identical cell parameter a of 3.647 Å, and interplanar distance of 5.889 Å. However, the c parameter can vary and be very large because of the variable offset between layers that gives origin to many polytypes.

In some cases, the unit cell size in the c direction may reach more than 700 Å! Moreover, in the same crystal several phases of polytypes may coexist. Palosz et al. [5] suggested that this stacking variety is due to the partial occupancy of the site by Sn and S in the lattice, and that it is a consequence of the versatile bonding nature of tin and sulfur, which gives rise to many stoichiometric and nonstoichiometric compounds as well as lattice-site deficient structures.

6.3 Triboxidation of metal sulfides

The tribological characteristics that make metal sulfides different from graphite are at least three:

- i. Metal sulfides' lubrication is not affected to the same extent by impurities such as humidity and air that make graphite more lubricating, but at higher temperatures when water is removed the lubricant effect decreases. This is due to the fact that, in the graphite case, water reduces the covalent bond degree between adjacent layers.

- ii. Metal sulfides are thermally oxidized in a temperature range of 300–600 °C. The oxides formed are usually harder than the corresponding sulfides providing a behavior transition with a consequent increasing of the coefficient of friction. This can counterbalance the loss of friction due to carbon-based lubricants. In addition, in many sulfides the substitution of sulfur with oxygen implies a change of the oxidation state of the metal element. For example, Mo(IV) sulfide easily forms Mo(VI) oxide. This change inevitably causes a considerable structure alteration, also when lamellar structure is preserved. On the other hand, the main (and final) product of graphite oxidation (the carbon-based solid lubricant) is the gaseous CO₂ which is released without any contribution to friction and causes a massive wear loss. Moreover, the sudden emissions of CO₂ can decrease friction between the sliding surfaces.
- iii. It is well known that the oxidation can be activated by friction through the negative ion-radical action mechanism (NIRAM) with considerably higher rates than the thermally activated reactions [6], thus making these reactions very sensitive to change of brake pressure and rotor speed, which creates a feed-in energy to speed up these chemical reactions. Indeed, the semiconductor nature of most sulfides can provide low energy electrons excited by friction work. These electrons intervene in the transition state formation by lowering the activation energy.

The whole reaction in the case of MoS₂ is the following:



According to NIRAM, electrons are released by friction work and can react to form an oxygen radical ion which attacks the sulfide framework. Dangling bonds also are formed and many radicals are present on the surface, apart from those described in Figure 6.6. Humidity also plays a role as an alternative to oxygen. The mechanism described by means of NIRAM theory involves the formation of a triboplasma.

The case of MoS₂ oxidation adequately illustrates the changes of structure. The orthorhombic and monoclinic phases of Mo(VI) oxides are called α-MoO₃ and β-MoO₃, respectively.

The orthorhombic phase is the most stable and probably is that formed during friction in air. α-MoO₃ is a lamellar solid and consists of a double layer of distorted MoO₆ octahedra. The adjacent layers are linked by weak van der Waals forces. The cell parameters are $a = 13.86 \text{ \AA}$, $b = 3.70 \text{ \AA}$, $c = 3.96 \text{ \AA}$ [7] and the layered structure of

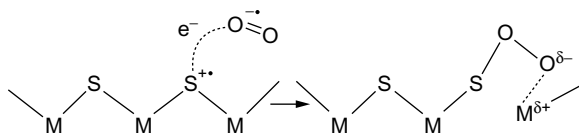


Figure 6.6 Possible mechanism of a metal sulfide oxidation in air under dry friction. The transition state (on the right) is the same as for the thermally activated reaction.

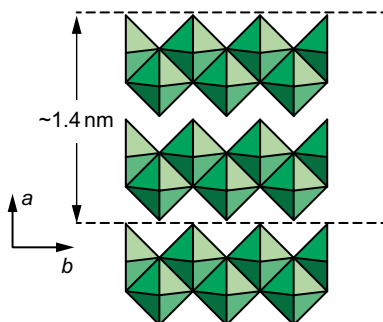


Figure 6.7 View of the α - MoO_3 structure along the a and b directions.

*K. Kalantar-zadeh, K. Galatsis, J. Tang, R. Kojima, M. Wang, V. Strong, K.L. Wang, A. Lech, A. Shailos, W. Wlodarski, R.B. Kaner, Synthesis of nanometre-thick MoO_3 sheets, *Nanoscale* 2 (2010) 429–433.*

zigzagged sheets made of MoO_6 octahedra is shown in Figure 6.7. The thickness of the double layer including a van der Waals gap is $13.86 \text{ \AA}$ ($\sim 1.4 \text{ nm}$). The interlayer gap is about $2 \text{ \AA}$, i.e., considerably lower than the $3.49 \text{ \AA}$ of MoS_2 , which will cause a less lubricating effect of the Mo(VI) oxide in comparison to the Mo(IV) sulfide.

6.4 Sb_2S_3 : A paradigm for all metal sulfides in brake applications

Antimony trisulfide is currently the most effective metal sulfide in the friction industry. This fact demonstrates that not only the lubricant effect is desired, but also the oxide formation and change of oxidation state of the metal element is a determining factor.

Sb_2S_3 crystallizes in the orthorhombic system. Each Sb atom is bound to three oxygen atoms forming a trigonal pyramid according to Figure 6.8. The cell parameters are the following: $a = 11.223 \text{ \AA}$, $b = 11.311 \text{ \AA}$, $c = 3.839 \text{ \AA}$ [8,9]. Some authors exchange the cell parameters although the values are quite similar. Moreover, the cell parameters vary with temperature passing from monoclinic below 20°C to orthorhombic. The material consists of ribbons of Sb_2S_3 (four for each cell) parallel to the c direction, which form chains of ribbon pairs Sb_4S_6 . The Sb and S of neighbors have distances in the range of 3.11 – $3.64 \text{ \AA}$. Each pair is weakly linked to the neighbor chain. This characteristic of forming weakly linked chains is what provides the lubricant properties.

The tribooxidation products can be antimony oxides containing both Sb(III) and Sb(V) . The main product Sb_2O_3 has an orthorhombic structure and forms $-\text{O}-\text{Sb}-\text{O}-\text{Sb}-\text{O}-$ chains that are linked through terminal oxygen atoms.

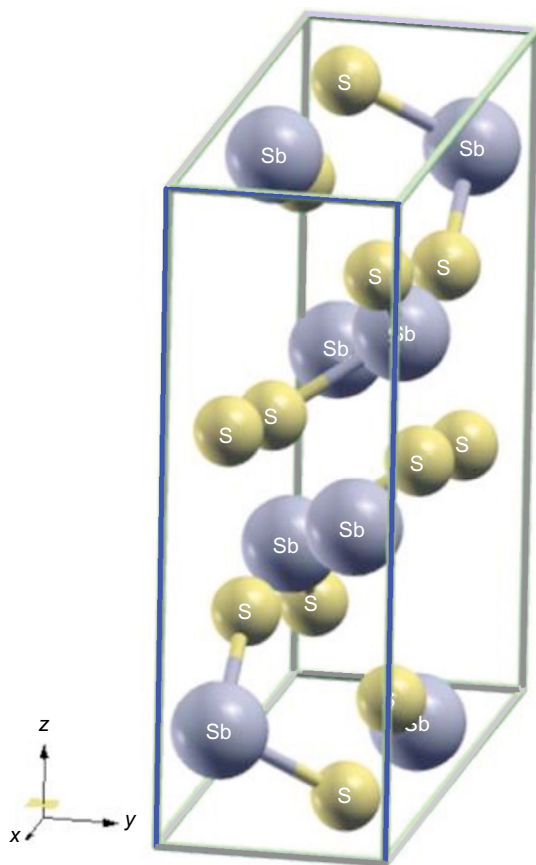


Figure 6.8 Crystal structure of Sb_2S_3 .

T. BenNasr, H. Maghraoui-Meherzi, H. BenAbdallah, R. Bennaceur, Electronic structure and optical properties of Sb_2S_3 crystal, Physica B 406 (2011) 287–292.

6.5 Synergy between sulfides and abrasives

The synergy between abrasives and sulfides is very interesting. In this regard, a study by Jang and Kim [10] on non asbestos organic NAO formulas showed that the best balance between ZrSiO_4 and Sb_2S_3 is with the ratio 1:1; in the specific case, the percent of the two variable components was 4 vol%. The coefficient of friction obtained is relatively stable and high enough with this ratio, with a maximum around 0.38 at 250 °C in a full-scale drag test [10].

This research report highlighted another relevant indirect effect of Sb_2S_3 , which is that of disk thickness variation (DTV). The blends with a higher content of Sb_2S_3 (up to 6 vol%) exhibited a lower brake torque variation (fewer vibrations) due to a lower DTV, since large amounts of the abrasive zirconium silicate causes a higher instability mainly due to the high coefficient of friction (see Chapter 5). The lowest wear was

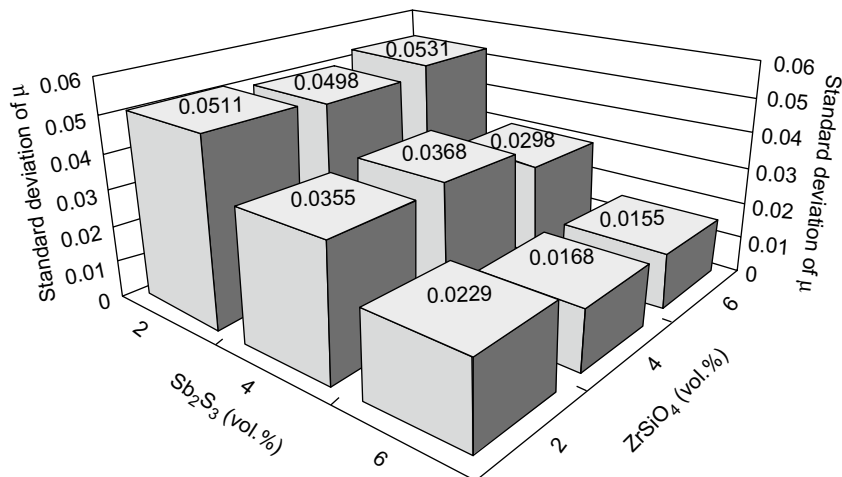


Figure 6.9 Stability of friction coefficient, represented as standard deviation of different μ values from 20 different stop conditions.

H. Jang, S.J. Kim, *The effects of antimony trisulfide Sb₂S₃ and zirconium silicate ZrSiO₄ in the automotive brake friction material on friction characteristics*, *Wear* 239 (2000) 229–236.

also obtained with the highest content of Sb₂S₃ at 6 vol% and the lowest one of ZrSiO₄. However, the most outstanding effect of Sb₂S₃ is the stabilization of the friction level, and in this case synergy can be found between sulfides and abrasives as in the case mentioned with ZrSiO₄.

Figure 6.9 exposes this effect quite clearly by reporting the standard deviation of the coefficient of friction during stop in different conditions. The lowest standard deviation was found again for the ratio 1:1 but with 6 vol% of both components. However, the effect of Sb₂S₃ on stabilization of the coefficient of friction is very marked, while that of ZrSiO₄ is much less and seems to be due to a sort of “cooperation” between the two materials.

This result suggests that Sb₂S₃ in the friction material plays an important role in improving friction stability [10].

The synergy between the abrasive and the sulfide can be understood in terms of surface modifications induced by the sulfide upon abrasive action. The mechanism can be depicted as follows: abrasives remove the oxide layer, exposing the metal surface, and then the sulfides are easily deposited due to their either lamellar or chain structure. At this point the sulfides are oxidized, and the oxides, less adhesive than sulfides, are removed again by abrasives or delamination after a limit thickness has been reached. In this way a protective action of the metallic surface is provided. Through this mechanism thermal DTV and cracks by thermal–mechanical fatigue are prevented (e.g., in commercial vehicles).

The stabilization of the coefficient of friction is obtained through a balance between adhesion and deformation forces that decrease the effect of variables such as speed and pressure, according to Equation (2.23):

$$\mu = \frac{\beta p + \tau}{p} = \beta + \frac{\tau}{p} \quad (6.4)$$

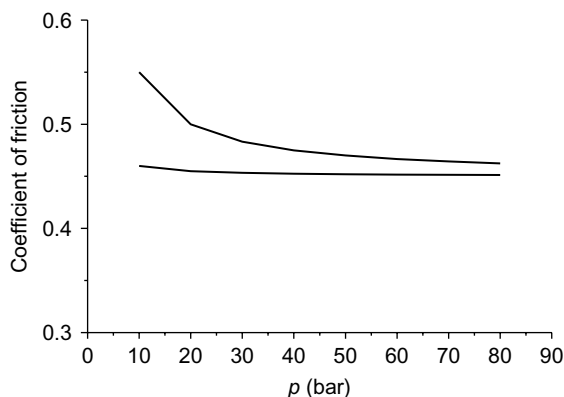


Figure 6.10 An example of sensitivity to pressure. In the upper curve τ was 0.1 bar and in the lower one 1 bar, while β was in both cases 0.45.

where both β and τ are terms linked to adhesion forces; however, β is correlated to the enlargement of adhesion due to deformation, and p is pressure. This equation expresses the sensitivity of the coefficient of friction to pressure. If the component that expresses the shear strength τ of the film of sulfide–oxide composite is low, the sensitivity to pressure would be less marked, because the steady value will be reached quickly. The term τ seems to depend mostly on the sulfides. The value of β will depend also on sulfides and the sliding surfaces' contact. This is a clear example of the balance between opposites that is sought to achieve adequate friction material performances. Figure 6.10 shows an example of sensitivity to pressure according to Equation (6.4).

It is interesting to notice the evolution of ratios among the components of a formula towards a lower sensitivity to both pressure and speed in a hybrid formula. The greatest benefit for the specific formula was found for ratios of sulfides:abrasives:metals of 0.42:0.17:0.41 as shown in the ternary diagram of Figure 6.11.

The speed sensitivity as function of the ratio between sulfides and metals for the formula development mentioned is reported in Figure 6.12 for a full dyno performance test. This graphic clearly shows that metal sulfides are more determinant than metals. However, a certain degree of cooperation and a compromise between the two main contributors to the tribofilm on the disk surface is reached. In fact, according to Figure 6.12, below a certain ratio of metals even the sulfide effect is faded.

Metal sulfides basically transfer metals from the friction material to the disk surface, acting as a lubricating soft and lamellar solid that favors the deposition and formation of a steady composite metallic tribofilm on the rotor surface, and it seems they do better than solid metals.

Evidence of the transfer film of Sb has been reported in many studies, and the low content of S found confirms the idea that a composite oxide layer is formed containing FeOx and even very small graphite/carbon particles [11]. The thermal properties of metal sulfide connected to their ability to be oxidized seem to be the determiners

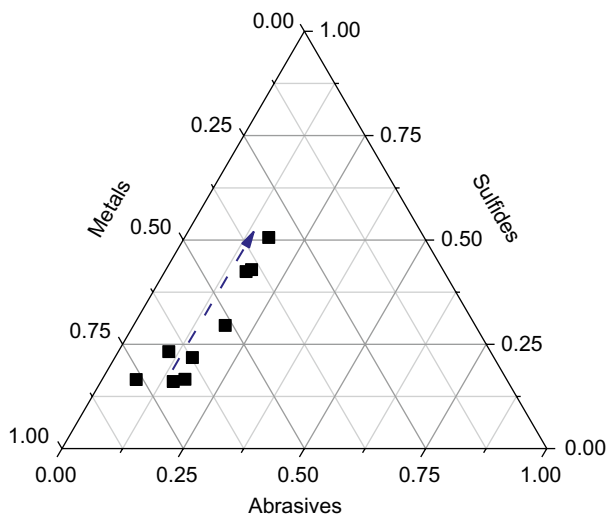


Figure 6.11 Ternary diagram showing the path of a formula optimization towards the sulfides' increasing (see the arrow).

of this effect. The differential scanning calorimetry of Sb_2S_3 (Figure 6.13) shows that there are two main transformations: the former around 300°C attributable to the exchange reaction between S and O to form Sb_2O_3 , the latter at 550°C to the oxidation of Sb(III) to Sb(V) to form Sb_2O_5 . These reactions when activated by friction can be faster and occur at lower temperatures. The thermal and tribochemical characteristics of metal sulfides make them the keystone of friction materials.

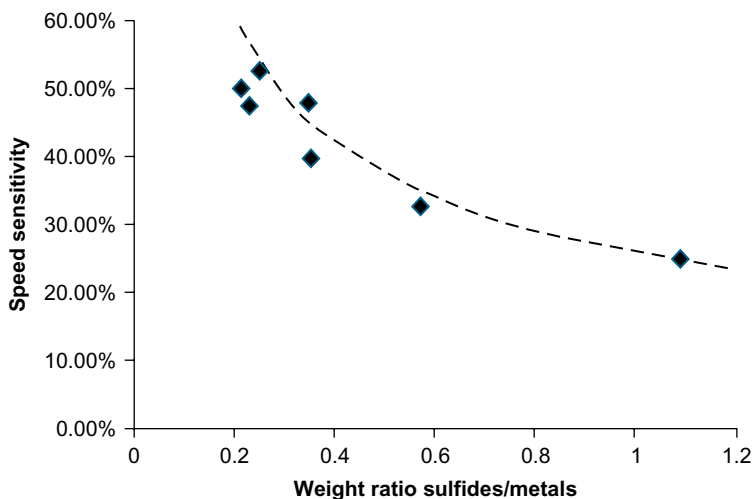


Figure 6.12 Speed sensitivity as function of the ratio between metal sulfides and metals.

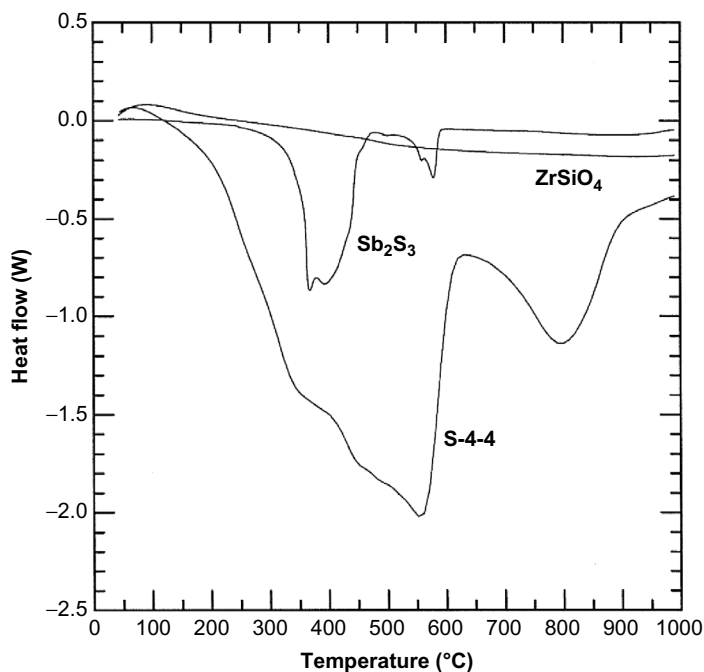


Figure 6.13 Differential scanning calorimetry curves for Sb_2S_3 , zircon silicate, and a NAO friction material containing both raw materials.

H. Jang, S.J. Kim, *The effects of antimony trisulfide Sb_2S_3 and zirconium silicate ZrSiO_4 in the automotive brake friction material on friction characteristics*, *Wear* 239 (2000) 229–236.

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7.1 Introduction

Carbon-based materials represent another important class of raw materials used in friction. They are used for different purposes, e.g., graphite is used for its lubricating properties. Coke is used because, being porous, it binds better to the resin matrix, is a mild abrasive and contributes to lowering the density of the brake pad. Carbon black is added together with rubber in small quantities. These carbon materials, although all are composed of carbon, are characterized by different degrees of crystallinity and different macro- and micromorphology, which affect all the physical properties. The basic structure is that of graphite with planes of honeycomb-arranged carbon atoms, spaced by an interplanar distance of about 3.35 Å. Each plane is shifted with respect to the adjacent one and follows the sequence ABA, as depicted in Figure 7.1. Although all the carbon atoms are in sp^2 hybridization, nevertheless this can give origin to a great variety of material macrostructures with almost identical basic microstructures. The unit cell parameters are $a=b=2.46$ Å (in-plane) and $c=6.70$ Å ($c/2$ is the interplanar distance).

Carbon materials can be either mineral or synthetic, such as the so-called synthetic graphite, which is produced starting from a “soft carbon,” i.e., a carbon material that is able to pass through a liquid or fluid phase, often called a *mesophase*. In this phase the macromolecules, precursors of graphite, are already aligned in a long-range order of the type of liquid crystals. Hard carbons cannot be transformed into graphite by simple heat treatment since the movements and reordering necessary are impeded by steric hindrance and/or cross-linking. An example of hard carbon is charcoal. Moreover, the thermal degradation of phenolic resins gives origin to a glassy carbon but not to graphite. Another aspect to be taken into account is that graphite is a highly anisotropic material with strong covalent σ bonds and delocalized π bonds in the graphene plane, quite similar to aromatic compounds, and weak interaction between adjacent graphene layers, although there is also a certain degree of covalent π bond between layers, which impedes sliding and allows stacking. For instance, it is noteworthy to point out that electrical and thermal conductivities are rather high within a graphene layer, but low in the c direction.

In recent years, after groundbreaking experiments on graphene and the consequent Nobel prize to Geim and Novoselov in 2010, most of the attention has been directed to the extraordinary mechanical properties of graphene that make it the strongest two-dimensional material. Moreover, graphene planes are indeed very flexible, so that it doesn't matter that under friction graphene layers will be oriented along the sliding direction in the matrix; in spite of the particle shape and their orientation in the friction material, they will finally be oriented with graphene layers parallel to the counterpart surface. Due to this situation, it is irrelevant to lubrication whether the particles are

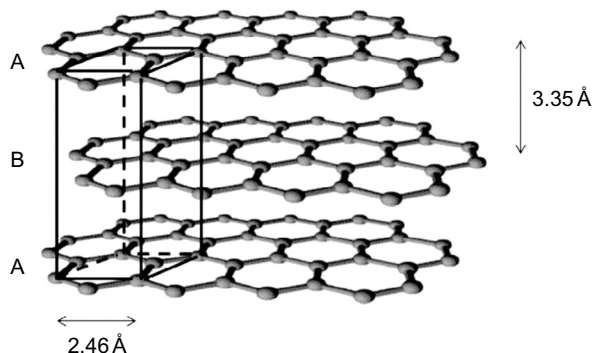


Figure 7.1 Graphite structure with the alternate plane stacking ABA and the unit cell.

a flaked shape or not. However, the macromorphology of particles can be important, mainly as regards incorporation into the resin matrix. Graphite thus exhibits two different ways to respond to external forces: slipping between stacks in the direction perpendicular to the crystallographic c axis, and being flexed along the c direction as the pages of a book. These two types of movement are well illustrated in [Figure 7.2a and b](#), respectively.

For this reason, the c direction is considered to be fundamental to define the graphite properties in relation to lubrication. In fact, a parameter that is important in determining the graphite properties is the size of the crystallite along the c direction L_c .

Graphite can be either synthetic or natural, and a great variety of morphologies are illustrated in the following sections. In addition, coke types, mainly obtained as a by-product of oil industry processes, can be seen as precursors of synthetic graphite, but in friction materials they have an important role almost independent from graphite, linked to their porosity and lower lubricity.

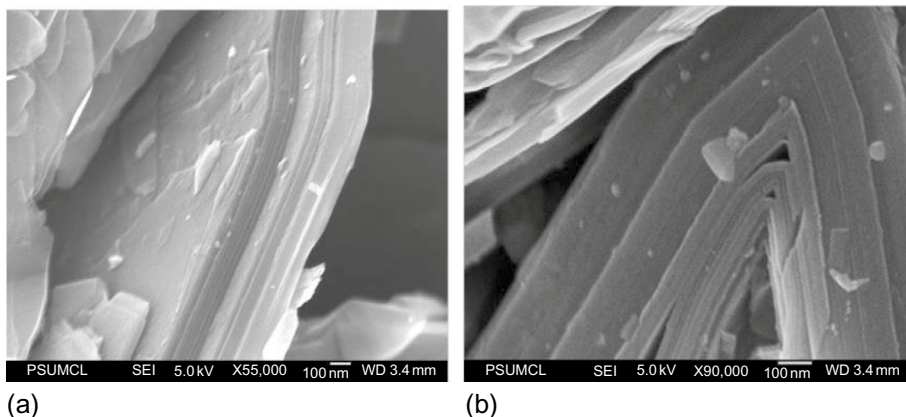


Figure 7.2 SEM images of graphite sheets doubled by external forces. (a) Slipping between planes previously overlapped; (b) flexion and doubling of stacked graphite sheets.

Courtesy of Asbury Carbons, NJ, USA.

Although the porosity of coke cannot be compared with that of activated carbon, it is much more important than that of graphite, which is accidental and due to interstices among crystallites.

Carbon materials are definitely fundamental components of friction materials, and their effect is tightly linked to sulfides for their lubricant properties. In the last few years, after the banning of copper in friction materials in certain US states since 2010, there have been efforts to partially substitute graphite for copper because of the high thermal conductivity of graphite, which is between 350 and $250 \text{ W K}^{-1} \text{ m}^{-1}$, although this decreases quickly with increasing temperature to values around $100 \text{ W K}^{-1} \text{ m}^{-1}$ at temperatures around 500°C , while the thermal conductivity of copper is around $400 \text{ W K}^{-1} \text{ m}^{-1}$ and is much less sensitive to temperature (almost stable above 100 K) and is isotropic. This fact made it difficult to substitute graphite for copper (without considering the mechanical and tribological properties), since copper will efficiently remove heat from the contact surface at contact temperatures that are typical in friction materials.

7.2 Natural graphite

Natural graphite can be divided into three main groups: vein, flake, and amorphous graphite. The three types of graphite can have different applications depending on purity and morphology. The crystallographic density of graphite is 2.26 g cm^{-3} ; higher densities can be due to impurities, while lower ones can be due to trapped porosity. The differences among natural graphite types can be due to several geological phenomena acting on carbon deposits in either metamorphic or igneous conditions, which can have a different origin, mainly biological [1].

7.3 Amorphous graphite

The name of “amorphous” graphite is a contradiction, since the term *graphite* can be applied only to the crystalline carbon material with honeycomb lattice. However, this term is used for the irregular shape of the lumps of this particular type of graphite, which is originated by localized contact metamorphism of coal seams (Figure 7.3).

Its degree of crystallinity is very low, and it could be more properly named *microcrystalline graphite*, i.e., a graphite with very low L_c , and for this reason looks dark black instead of silver gray like the other, more crystalline graphites. In this type of graphite material, graphitization could not be extended either because of the lack of long-range order in the carbon precursor or because energy in the metamorphic process was not sufficient to proceed further. In any case, there is a convergence to the flake morphology at a microscopic level, as can be seen in Figure 7.4.

Moreover, it contains and is associated with other minerals, ashes or clays, so that the carbon content can be as low as 75%. Its applications are limited to those which can tolerate a certain content of abrasives.

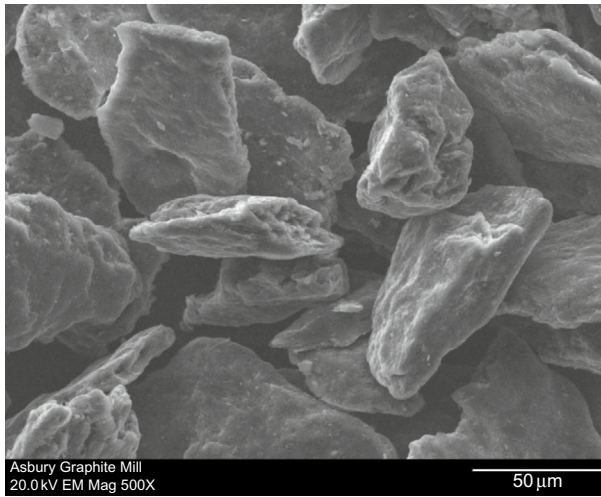


Figure 7.3 Particles of amorphous graphite.
Courtesy of Asbury Carbons, NJ, USA.

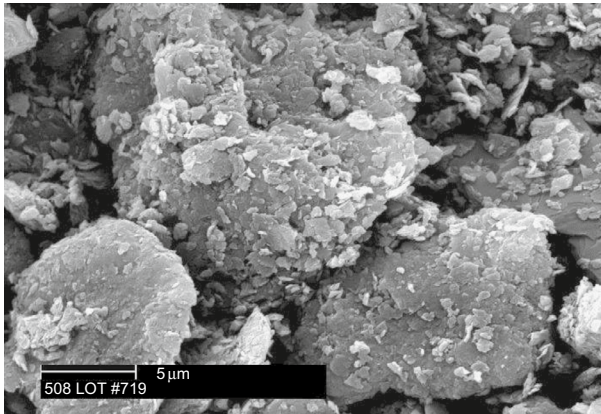


Figure 7.4 Convergence to flake morphology of amorphous graphite at a microscopic level.
Courtesy of Asbury Carbons, NJ, USA.

7.4 Natural flake graphite

Flake graphite is the most commonly known case of natural graphite; with the exposition of the pinacoid basal plane perpendicular to the c direction, it is a high grade metamorphic mineral, i.e., generated at both high pressures and temperatures around 1 GPa and 750 °C, respectively. The purity can vary from 90% to 98%; unfortunately, it cannot be lower due to the intercalation minerals that cannot be removed by floatation. An example of flake graphite is shown in [Figure 7.5](#). The flaky or platy morphology

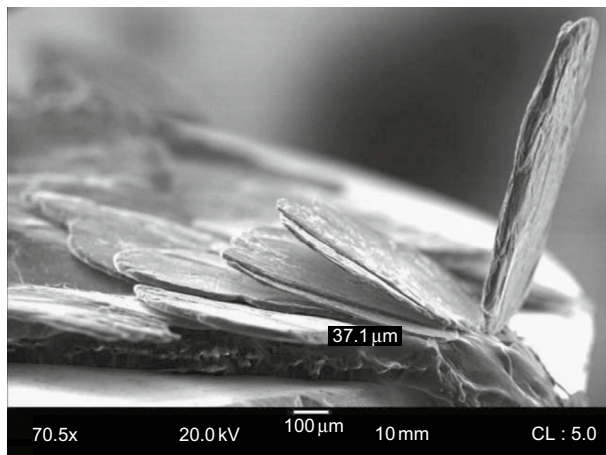


Figure 7.5 SEM image of flake graphite.
Courtesy of Asbury Carbons, NJ, USA.

can be considered the basic microstructure of graphite, and the size of these regions really differentiates one type from another. It is noteworthy to point out that, in the case of flake graphite, L_a (the in-plane size of the crystallite) is much higher than L_c (the stack's thickness).

7.5 Vein graphite

Vein graphite is the most interesting case of natural graphite because of its origin and mechanism of formation. In fact, the formation mechanism resembles that of a chemical vapor deposition: a supercritical pyrolytic carbon fluid is supposed to be formed, where conditions allow it, which then is deposited at lower pressures and temperatures in spaces and interstices available in previously formed country rocks. The degree of contamination is very low for this case, since the formation of the vein graphite is subsequent to that of rocks, so that purity is usually between 94% and 99%. All the commercially available vein graphite currently hails from Sri Lanka, and for this reason Ceylon graphite has become synonymous with vein graphite. As for the other cases of graphite, vein graphite morphology tends to approach the flake one at the microscale (see [Figure 7.6](#)). This confirms that the main difference among graphite types is only a scale factor, apart from purity. Concerning the temperature stability, it can be said that the graphite types with a more extended (large scale) flake morphology will be slower oxidized because they will have a smaller surface area and less active exposed active edges, thus decreasing the rate of oxidation. However, cleavage as well as fractures under friction can substantially modify this situation.

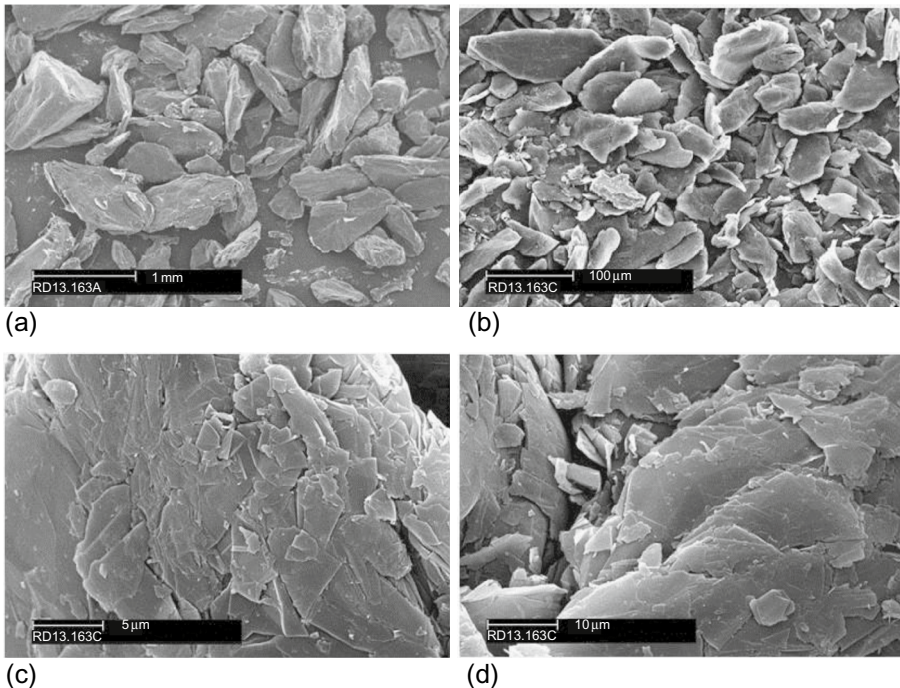


Figure 7.6 Convergence to flake morphology for vein graphite. SEM images: at low magnifications (a,b) it is not possible to observe the flake structure. Increasing magnifications to c) and d) it is possible to observe that the microstructure converge to a flake one.

Courtesy of Asbury Carbons, NJ, USA.

7.6 Synthetic graphite

Synthetic graphite is produced from graphitizable carbon forms, i.e., the aforementioned soft carbons, which passed through a mesophase in their thermal history. The basic raw material is the calcined petroleum coke, and 20% coal tar pitch is used as a matrix binder. The coal tar pitch will pass through the mesophase during a first baking process, while the whole graphitization process occurs at temperatures higher than 2800 °C in an Acheson-type furnace, for example. The final product is composed of graphitized petroleum coke and graphitized coal tar pitch.

This kind of graphite is highly conductive and is produced in large electrodes, especially in metallurgy. It is very appreciated in friction because it is a standardized product. Its purity will depend on the purity of the starting petroleum coke used; needle coke has less impurities. The final product keeps the macromorphology of the original coke, and when ground tends to resemble flake graphite. However, the reflectance of the graphitized product is much higher, with a silver-like effect. As with natural graphite, there is a convergence towards flake morphology at the microscopic level (see [Figure 7.7](#)).

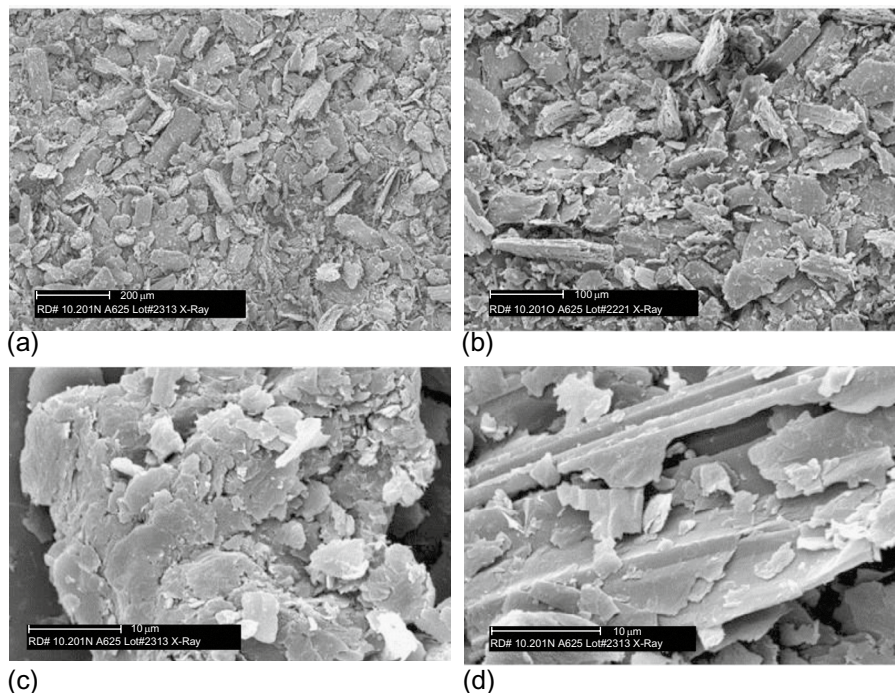


Figure 7.7 Convergence towards flake morphology of synthetic graphite. Courtesy of Asbury Carbons, NJ, USA.

7.7 Coke

Coke is the other carbon material that enters into friction formulas—carbon black enters in low quantities only for rubber use in friction materials—in an amount that can vary from 5 to 20 wt.%. It is considered a mild abrasive or, better said, a less lubricating form of sp^2 carbon. However, it can be considered a turbostratic material, not well stacked in the c direction but well formed in a with large sheets developed. The L_c parameter is quite low for cokes, being in the range of 20–40 sheets, and the interplanar distance, around 3.45 Å, is higher than that of graphite.

Petroleum coke, also called “pet coke,” may be obtained by heat treatment of oil residua after distillation, and finally the green coke is calcined to remove the volatile substances till present. The purity is usually in the range of 97–99%. Metallurgical coke (met coke) is obtained by destructive distillation of bituminous coal. Met coke has a glassy aspect and a porous microstructure due to the loss of gases during polymerization, and the carbon content fluctuates between 88% and 92% depending on the feedstock. Pitch coke is the result of the destructive distillation of coal tar pitch, which is a by-product of the distillation of bituminous coal. Since coal tar pitch is condensed from the gas phase it has low impurities, low sulfur and vanadium.

Calcined needle coke is a type of petroleum coke, with an acicular morphology visible by the naked eye. It is more crystalline and anisotropic than other cokes, with an extended growth in the a direction, and for this reason it is a good candidate to be graphitized.

It is also interesting to mention fluid bed coke, i.e., coke obtained by fluid bed cracking reactors, which is a case of isotropic coke with round-shaped particles.

Summing up, in spite of being sp^2 hybridized, cokes differ from graphite for the low degree of crystallinity especially in the c direction. They can be highly anisotropic such as needle coke (see a detail in Figure 7.8a), i.e., well developed in the plane directions but not in c (see Figure 7.8b), or highly isotropic as fluid bed coke, which is another type of petroleum coke, or the pet coke shown in Figure 7.8c. They can be either very or poorly porous depending on the gas release process during production, and harder or softer particularly depending on impurities. The porosity is especially macroporous as shown in Figure 7.8d, not comparable with activated carbon but enough to favor anchoring to the resin matrix. In some cases, silica content in metallurgical coke can be so high as to affect wear considerably. It is noteworthy to point out that in the case of coke, there is no convergence to flake morphology for the different types.

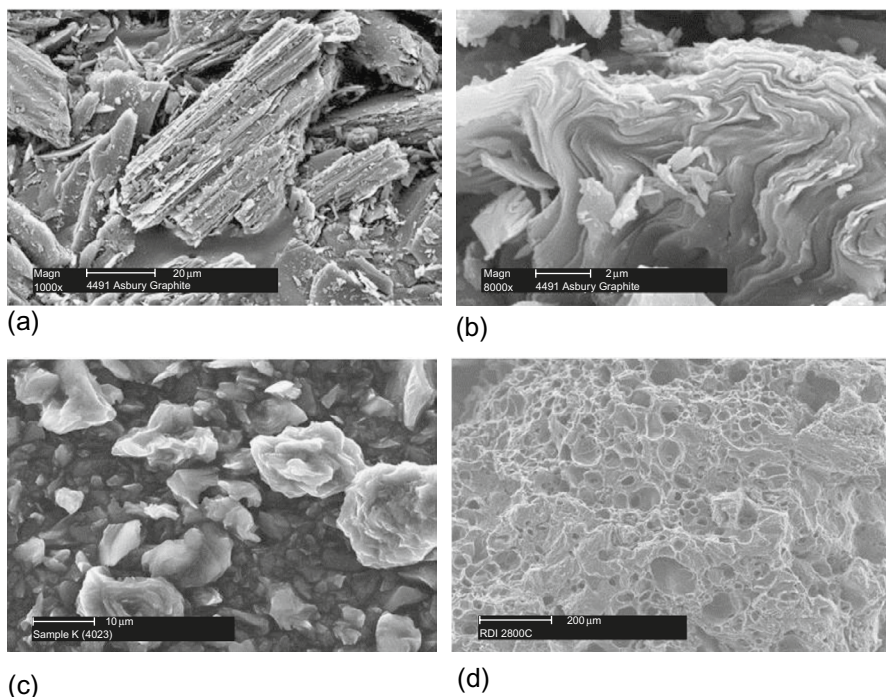


Figure 7.8 (a) Needle coke; (b) a detail of a needle coke particle; (c) isotropic petroleum coke; and (d) an example of macroporosity of coke.

7.8 Friction behavior of carbon materials

Graphite seems to work well coupled with metal sulfides in a balanced ratio. For a non asbestos organic NAO formula Kim et al. found as an adequate ratio 6 wt.% of graphite to a 3 wt.% of antimony trisulfide [2]. They found a reduced pressure sensitivity in the interval of 1–7 MPa, and a good stability for speeds between 10 and 100 km h⁻¹ in a drag test with a real brake but an inertia of 0.44 kg m². Similar results were found by Cho et al. underlining the synergy between antimony trisulfide and graphite in stabilizing the coefficient of friction [3]. They attributed this behavior to the friction film. However, no clear evidence was presented.

The particle size seems to be important in increasing stability and decreasing the sensitivity to both speed and pressure. In a study the smallest size tested (21 μm) was found to improve these qualities [4]. This size effect is also emphasized on hot spot appearance. Once more, the small size particles of 21 μm with a higher thermal conductivity (2.83 W m⁻¹ K⁻¹) retard the appearance of hot spots and reduce the phenomenon of thermal localization [5].

A possible effect of sulfides is that, since they are oxidized, they can prevent the destructive oxidation of graphite to a certain extent at the high temperatures of the contact surface, thus favoring the adhesion of the graphite basal plan on the contact layer (either pad or rotor) composed of mixed oxides, including the oxidized sulfide. Graphite will moderately lubricate in this case instead of being quickly removed as worn debris. In support of this hypothesis, there is the range of oxidizing temperatures of Sb₂S₃, which is between 400 and 600 °C, before the oxidizing (combustion) of graphite beginning at 700 °C. On the other hand, MoS₂ is oxidized around 600 °C, but MoO₃ sublimates around 700 °C, just before graphite oxidation, as shown in the thermal gravimetric curves of Figure 7.9.

This fact may explain why the behavior of MoS₂ is so different from that of Sb₂S₃ with graphite. The sublimation of MoO₃ causes a similar effect to that of graphite loss due to combustion: a gas film is produced which drastically decreases the coefficient of friction, and the material loss is not replaced by another product. This is reflected in friction tests, where almost no effect of MoS₂ was found in stabilizing friction or in decreasing the fading, as shown in Figure 7.10.

It is noteworthy to point out that this is a synergistic effect, since graphite without sulfide or vice versa does not efficiently decrease either speed or pressure sensitivity.

Two aspects seem to be important with graphite: small particle size and synergy with metal sulfides, especially those whose oxides sublime after graphite oxidation. The effect of small particle size is probably related to a better distribution of the lubricant on the contact surface. On the synergistic effect, one should remember that it is well known that at the edges of the graphene layers carbon is bonded to heteroatoms such as oxygen and hydrogen. The edges are very unstable and for this reason tend to react, for instance with oxygen in the air. Hydroxide groups and carbonyls are bonded to the edge terminal carbons; in turn these functional groups may further react with the metal sulfide bonding graphite with the oxidized sulfide adhered on the contact surface. Figure 7.11 depicts the oxygen bonded to edge carbon atoms of graphite layers, which may react with metal sulfides to bond the two materials.

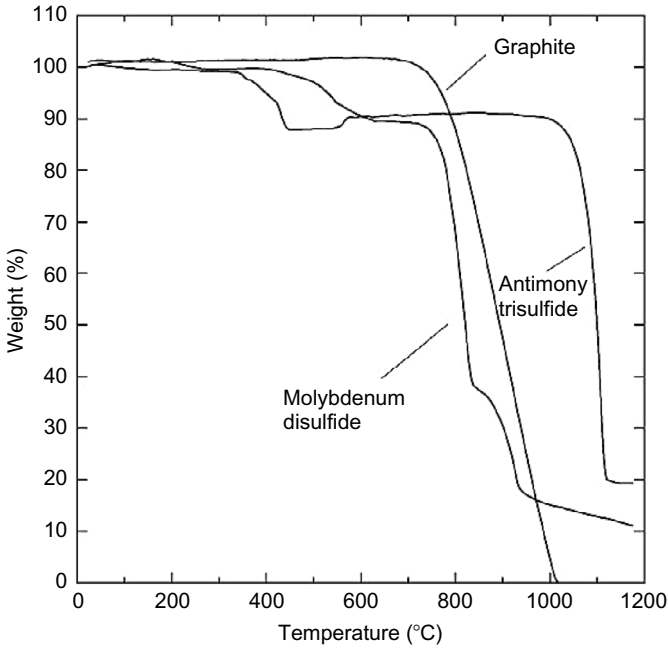


Figure 7.9 TGA curves of MoS_2 , Sb_2S_3 , and a graphite sample.

M.H. Cho, J. Ju, S.J. Kima, H. Jang, Tribological properties of solid lubricants (graphite, Sb_2S_3 , MoS_2) for automotive brake friction materials, Wear 260 (2006) 855–860.

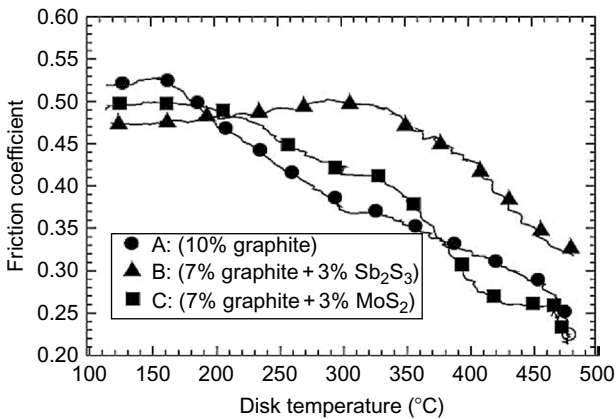


Figure 7.10 The change of the coefficient of friction as a function of disk temperature during the drag test for specimens A, B, and C.

M.H. Cho, J. Ju, S.J. Kima, H. Jang, Tribological properties of solid lubricants (graphite, Sb_2S_3 , MoS_2) for automotive brake friction materials, Wear 260 (2006) 855–860.

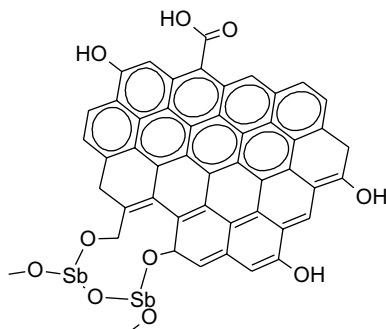


Figure 7.11 An oxidized graphene lamella bonded to the metal oxide derived from the sulfide. The oxygen atoms bonded to the edge carbon atoms are those which react with the metal sulfide.

This mechanism hypothesis can be summed up in the following way: (a) metal sulfides adhere to the disk surface due to their soft lamellar or chain structure; (b) sulfides are generally oxidized keeping quite soft characteristics; (c) graphite oxidized edges bind to the metal sulfide/oxide and slip; (d) graphite is finally destroyed by oxidation or incorporated into the composite film as nanoparticles.

This possibility is better known due to the recent studies focused on graphene that showed evidence for the reaction of the edge dangling bonds of graphene with metal oxides [6].

In the described case, the synergy between graphite and metal sulfides is interpreted in terms of a direct interaction between graphite and sulfides (bonds are formed). However, how this interaction causes the observed final friction properties is still open to discussion. It can be due substantially to two different phenomena: (i) prevention of graphite oxidation by the metal sulfide which occupies the most active sites of graphite or (ii) anchoring the basal graphite plane to the metal sulfide (oxide) to favor interplanar slipping.

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Abrasives, ceramic, and inorganic materials

8

8.1 Introduction

The complexity of the effects of abrasives is often neglected in friction materials. They are considered to be responsible for a direct increasing of the coefficient of friction. However, their effect is much more complex, involving removal of disk surface oxides and mixing in the composite film. Although the term “abrasive” is generally used for an inorganic compound with a hardness much higher than that of the disk, in this chapter many inorganic and ceramic materials are also included although their hardness is not significant, because they share with abrasives some of the following characteristics: either strong covalent or ionic bonds with at least a non-metallic element, low adhesion forces, brittleness, in many cases surface reactivity, low thermal conductivity, low electrical conductivity, high melting temperatures, and thermal transformations only at relatively high temperatures (above 500 °C). Strong abrasives such as alumina, e.g., corundum, and silicon carbide are generally used in small amounts around 0.2 up to 2 wt.%, while mild abrasives, such as zirconium silicate and magnesium oxide, are used in larger quantities. Polymorphism is often neglected by formulators; however, alumina, for example, exhibits many phases such as α (corundum), θ , γ , etc. Other compounds such as mica and vermiculite are usually considered to be fillers used to decrease density and reduce noise. Calcium carbonate, calcium fluoride, and barium sulfate are the most common “inert” fillers; however, their effect is too often neglected, especially in the so-called “ceramic friction materials.” In the last few years, calcium carbonate has acquired renewed attention because of the decomposition from 700 °C to calcium oxide, which absorbs a large amount of heat from the contact surface. This chapter deals with the tribological properties of abrasives, also considering that oxides and especially hydroxylated ones become more lubricating, particularly with increasing temperature. Size and shape have an important role in the tribological properties of abrasives, especially for wear. Smooth and small particles favor low wear and more stable tribofilms. For instance, the development of suitable nanoabrasives opens the door to achieving very low wear, improving friction performances at the same time. Ceramic and glass fibers, as well as mineral fibers, have been neglected because they share many properties with other abrasives, and the properties directly related to their fiber nature will be discussed under polymeric fibers in Chapter 10.

8.2 Aluminum oxide

Aluminum oxide will be considered as a paradigmatic abrasive for its variety in morphology and its phases, which illustrate the main aspects to be taken into account for abrasives. It was always a common ingredient in friction materials, especially α - Al_2O_3 , also called alumina. It is the hardest material after diamond on the Mohs scale. In the field of friction, many other terms are circulating, such as *fused alumina*, *calcined alumina*, etc. All these terms refer to α - Al_2O_3 ; however, calcination of aluminum hydroxide and the alumina melted (fused) by electrofusion lead to different morphologies (bubble, acicular, etc.) which may acquire a certain interest in friction, since shape is fundamental in abrasive effects. The forms can vary from tabular to angular. Aluminum oxide is an ionic material. The most important, and common, polymorphs are denoted α , γ , θ , and κ . The old β - Al_2O_3 was discovered to be a compound containing Na. In addition to these, there are reports on more than 20 other minor crystalline phases.

The phase transformations from aluminum oxide minerals are reported in Figure 8.1.

The α phase is the thermodynamically stable polymorph and occurs naturally as corundum or sapphire, while the other phases are metastable in bulk form (but can still be produced in certain processes where thermal equilibrium is not reached, e.g., thin film growth). The differences in properties between the phases make them important in different applications. For example, the α and κ phases are widely used as wear-resistant coatings due to their high hardness and thermal stability, while γ - and θ -alumina are more suited for catalytic applications due to their lower surface energies, leading to larger active surface areas available for catalytic reactions.

The basic structure of aluminum oxide phases are oxygen hexagonal close packed planes stacked in the c -direction, where Al^{3+} ions occupy either tetrahedral or octahedral interstitial sites with some vacancies depending on the phase. However,

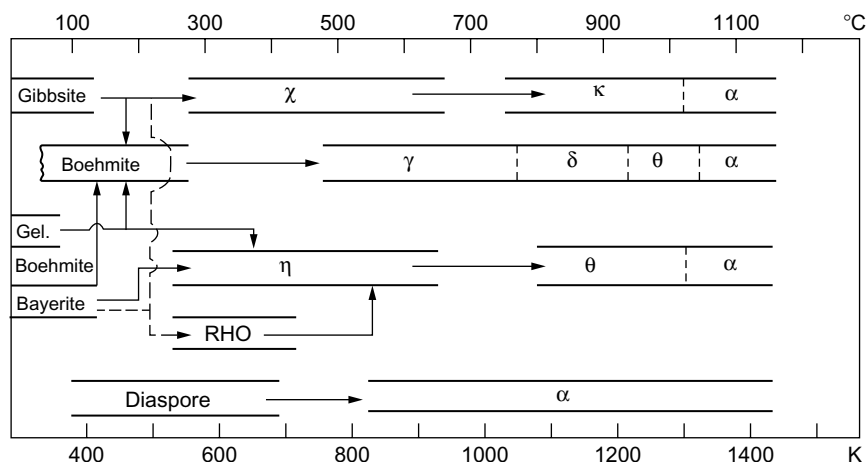


Figure 8.1 Thermal transformation sequence of the aluminum hydroxides.

P. Souza Santosa, H. Souza Santos, S.P. Toledo, *Standard transition aluminas. Electron microscopy studies, Mater. Res. 3 (2000) 104–114.*

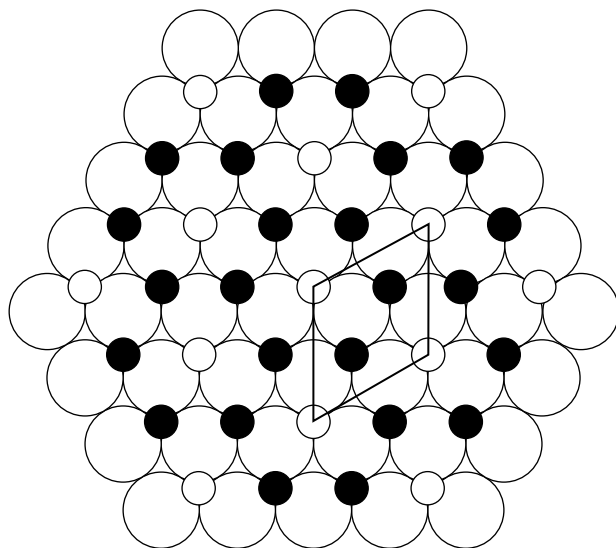


Figure 8.2 Schematic drawing of the first layer in the α -alumina structure.

α -alumina is the only stable alumina phase at all temperatures. It has a trigonal lattice and is usually described as ABAB stacking of oxygen planes along the c -direction with Al ions filling two-thirds of the octahedral interstitial positions (see Figure 8.2).

Apart the very different XRD patterns obtained from the several possible phases (as shown in Figure 8.3) [1], it is interesting to see how alumina morphology can vary within the same phase depending on the synthesis route, the precursors or milling methods, as shown for two cases of α - Al_2O_3 in Figure 8.4a and b [2]. In the (a) case the platelet morphology can be observed, while in the (b) case a coral-like morphology is obtained.

Other morphologies can be obtained, such as spherical, etc. This case well illustrates the difficulties of predicting the behavior of abrasives only on the basis of composition, either the crystalline phase or nominal hardness in contrast to the lubricants whose behavior is poorly affected by morphology and size.

Another aspect to be taken into account is reactivity, since the Al_2O_3 surface can be hydroxylated in the presence of moisture and dehydroxylated thermally, according to Equation (8.1):



8.3 Zirconium silicate and garnets

Zirconium silicate, also known as zircon, belongs to the family of nesosilicates, as garnets, and is another abrasive with mild features (Mohs hardness is around 7.5) and relatively high density ($4.6\text{--}4.7\text{ g cm}^{-3}$), which is used in friction materials with variable morphologies from sharp edges to smooth round-shaped particles. The generic formula of zircon

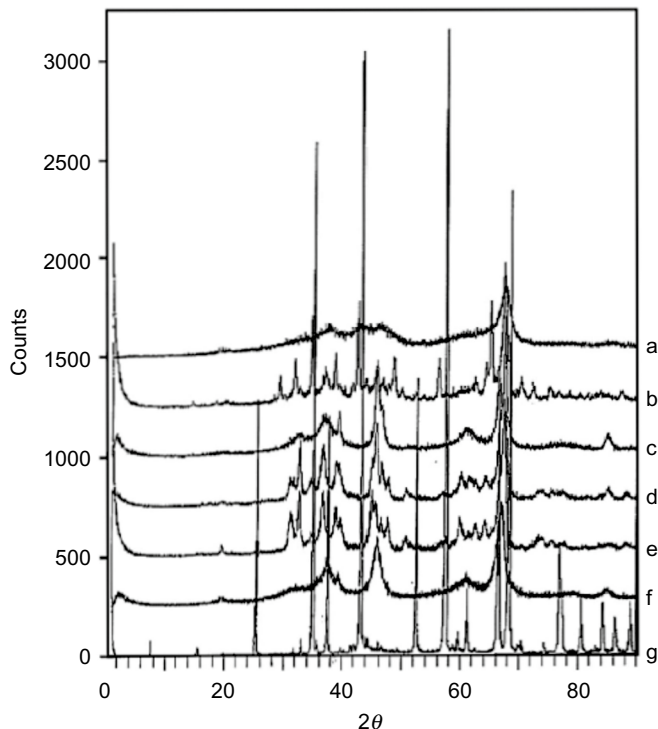


Figure 8.3 X-ray diffraction powder curves of: (a) χ - Al_2O_3 ; (b) κ - Al_2O_3 ; (c) γ - Al_2O_3 ; (d) δ - Al_2O_3 ; (e) θ - Al_2O_3 ; (f) η - Al_2O_3 ; (g) α - Al_2O_3 .

P. Souza Santosa, H. Souza Santos, S.P. Toledo, Standard transition aluminas. Electron microscopy studies. Mater. Res. 3 (2000) 104–114.

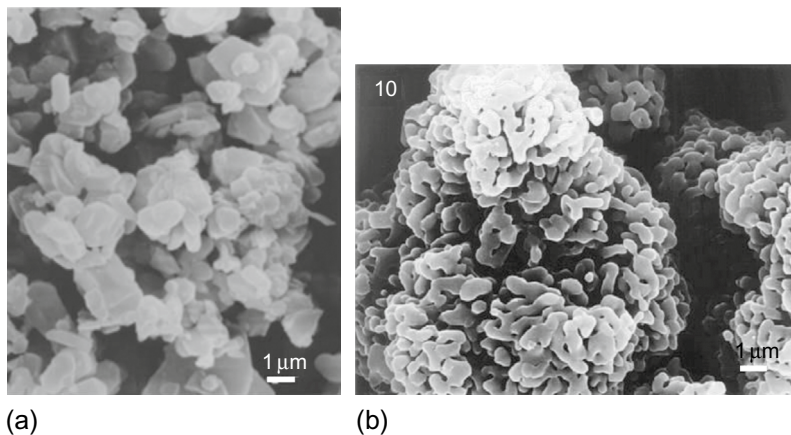


Figure 8.4 Two cases of different morphologies of α - Al_2O_3 due to different precursors and processes. (a) ALCOA 2011 [1]; (b) synthesized from aluminum hydroxyacetate.

P.K. Kiyohara, H. Souza Santos, A.C. Vieira Coelho, P. De Souza Santos, Structure, surface area and morphology of aluminas from thermal decomposition of $\text{Al}(\text{OH})(\text{CH}_3\text{COO})_2$ crystals, An. Acad. Bras. Ciênc. 72 (2000) 471–495.

is $(\text{Zr}_{1-y}\text{M}_y)(\text{SiO}_4)_{1-x}(\text{OH})_{4x-y}$, where M is a Zr substituent, and the chemical formula is ZrSiO_4 . When it has a mineral origin zircon may contain significant impurities of Hafnium (up to 4%), but it can be also synthesized from silica and zirconia. It has a high melting point around 2500°C . The principal structural unit in zircon is a chain of alternating edge-sharing SiO_4 tetrahedra and ZrO_8 triangular dodecahedra extending parallel to c (Figure 8.5) [3]. Similar chains occur in garnet (Figure 8.6), extending in three mutually perpendicular directions, but they are cross-linked by YO_6 octahedral as well as by XO_8 dodecahedra. In zircon octahedral voids are present but contain no cations (Figure 8.6). The structural similarities of zircon and garnet account for their similar hardness, density, and high refractive indices.

The mean bond angle at oxygen is 120° in zircon, indicating that its orbitals are sp^2 hybridized, leaving a lone pair perpendicular to the planar array available to form a double bond with Si. In garnet oxygen is four-coordinated by one Si, two (X^{2+}) cations and one (Y^{3+}) cation, suggesting a sp^3 hybridization of oxygen orbitals, with no lone pairs available for double bonding. These structure differences also account for the main differences in physical properties between the two materials.

It is noteworthy to point out that nesosilicates suffer phase and structure change induced by high pressure (more than 10 GPa), which implies, at pressures greater than 16 GPa, a change of Si coordination to four to six oxygen atoms and shortening of the Si–O bonds with a significant volume reduction [4]. The mentioned stresses unlikely may be reached on the contact junctions between pad and rotor.

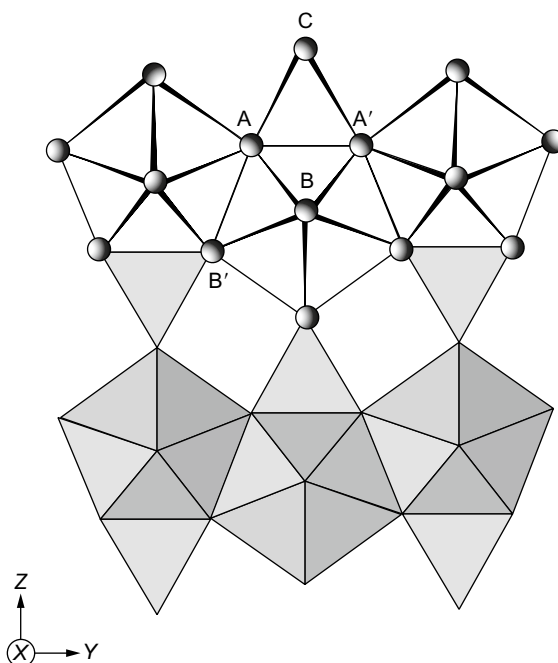


Figure 8.5 The chains of alternating edge-sharing SiO_4 tetrahedral and ZrO_8 triangular dodecahedra extending parallel to c and joined laterally by edge-sharing dodecahedra.

Reproduced from K. Robinson, G.V. Gibbs, P.H. Ribbe, *The structure of zircon: a comparison with garnet*, *Am. Mineral.* 56 (1971) 782–790.

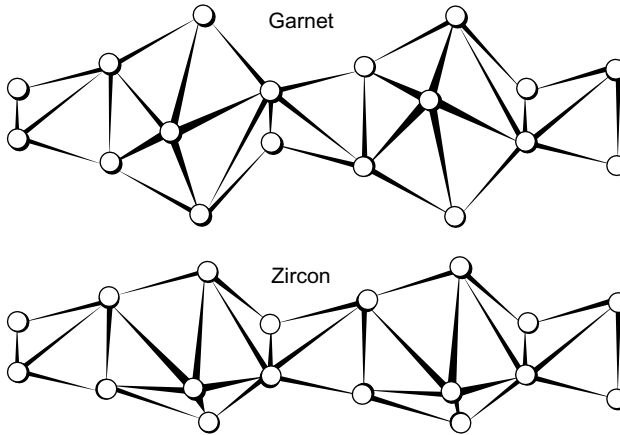


Figure 8.6 A comparison of the alternating edge-sharing tetrahedra and dodecahedra chain in zircon with similar chains in garnet.

Reproduced from K. Robinson, G.V. Gibbs, P.H. Ribbe, *The structure of zircon: a comparison with garnet*, *Am. Mineral.* 56 (1971) 782–790.

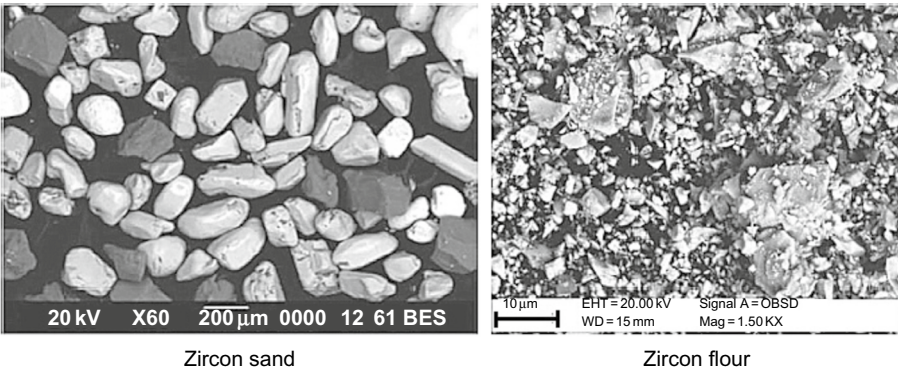


Figure 8.7 SEM images of zircon sand (round shaped) and zircon flour (angular).

S. Routray, R.B. Rao, *Beneficiation and characterization of detrital zircons from beach sand and red sediments in India*, *J. Miner. Mater. Charact. Eng.* 10 (2011) 1409–1428.

The two typical morphologies of zircon are called *sand* (round shaped) and the so-called *flour* (angular) with sharply different behaviors (Figure 8.7) [5].

8.4 Magnesium oxide

Magnesium oxide (MgO) is a white hygroscopic mineral known as periclase. In contact with water it forms:



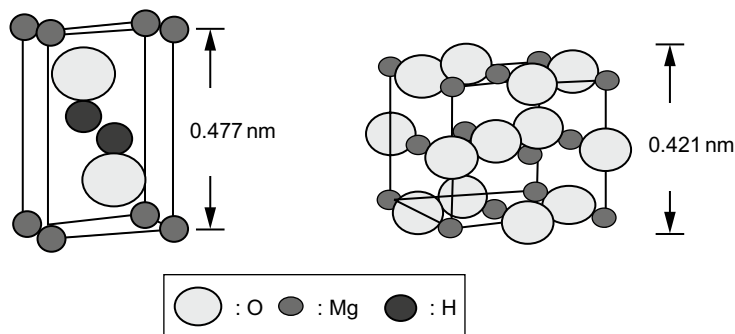


Figure 8.8 Structure of $\text{Mg}(\text{OH})_2$ (left) and that of MgO (right).

Heating over 300°C will revert the reaction (8.2) [6]. The dehydration heat is 81.06 kJ mol^{-1} . Tribochemical water desorption will change the tribological characteristics of the material since structural changes occur. Increasing the temperature a sudden recrystallization from hexagonal $\text{Mg}(\text{OH})_2$ to cubic MgO occurs through intermediate structures, accompanied by cracking of the crystal as the crystal structure stress is exceeded. The structure shrinkage changes from $\text{Mg}(\text{OH})_2$ to MgO as shown in Figure 8.8.

Moreover, hydrated magnesium oxide is a practical adjuvant to phenol–formaldehyde resin cross-linking through the adsorbed water or hydroxide that activates Hexa molecules. It is also useful as well as CaO to create a basic pH environment to avoid sticking by preventing oxidation of either steel fiber or gray cast iron of the disk.

8.5 Calcium carbonate

Calcium carbonate is found in three forms: calcite, aragonite, and the very rare vaterite. Calcite is the most stable polymorph with hexagonal structure, and can have a great variety of particle morphologies. Aragonite, which evolves spontaneously to calcite, is orthorhombic. The structure of calcite made of layers of CO_3^{2-} with interposed Ca^{2+} ions is depicted in Figure 8.9.

Aragonite crystallizes in an orthorhombic system with characteristic acicular particles, and is less stable than calcite. The morphology of calcite can vary depending on the feedstock and milling, a morphology type is shown in the SEM image of Figure 8.10 [7].

Both materials are soft in the Mohs scale and classified near 3. The most remarkable characteristic of calcium carbonate is that it decomposes at temperatures higher than 800°C to form CO_2 and CaO , a totally reversible reaction due to the presence of CO_2 in air, according to the reaction:



Moreover, CaO can react with humidity and form the hydroxide, another reversible reaction activated by heat, as for MgO in Equation (8.2). Despite the apparent high temperature of transformation, the transformation can occur by a triboreaction mechanism

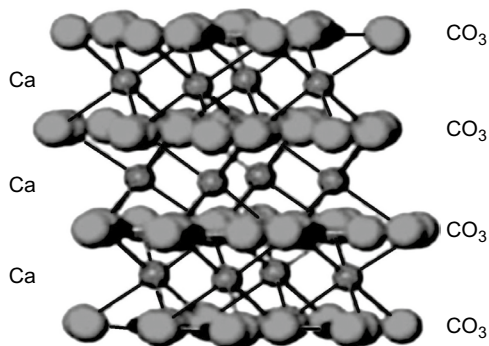


Figure 8.9 Calcite structure: layers of CO_3^{2-} with interposed Ca^{2+} ions.

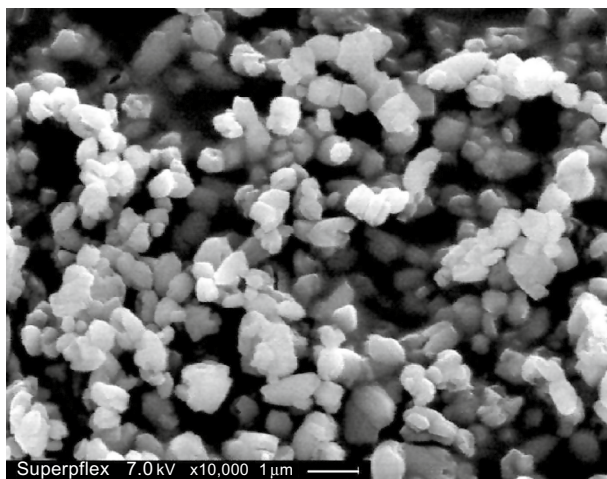


Figure 8.10 SEM image of calcite particles.

W.C.J. Zuiderduin, C. Westzaan, J. Huétink, R.J. Gaymans, Toughening of polypropylene with calcium carbonate particles, Polymer 44 (2003) 261–275.

that apparently lowers the energy barrier. This reaction, as with many of the ceramics otherwise classified as fillers, absorbs a considerable amount of heat. The heat of the decomposition reaction of Equation (8.3) is $177.8 \text{ kJ mol}^{-1}$ [8], equivalent to 1.84 eV per electron. This energy is in the range of the triboelectrons' energies, which are supposed to be the activators of tribochemical reactions [9]. The most interesting fact is that the reaction is reversible and the carbonate is re-formed by reaction with CO_2 in air.

In fact, all the decomposition reactions can be efficient heat removers, and dehydration is the most typical one. By reaction with humidity in air, Ca(OH)_2 can be formed and the decomposition reaction, activated by friction, can remove about 109 kJ mol^{-1} . The mass loss due to this decomposition is considerable and can reach the maximum value of 44% causing stresses and strains in the material, or volume changes. This fact prevents the use of large amounts of CaCO_3 , in order to avoid surface cracks during use.

Heat removal can have a relevant role in stabilizing the coefficient of friction, by removing the heat produced in the friction interface in order to avoid the decay typically due to the iron oxide layer and gas by-product formation. Moreover, hydroxides, hydrated silicates, and carbonates act as flame retardants, preventing the oxidation of both organic components, such as resin, and metals from removing the necessary heat. This effect is very important considering the general poor thermal conductivity of ceramics (abrasives), which can lead to high flash temperatures creating many new asperity contacts and increasing wear. Therefore, it is important to combine stable abrasives (low hydrated oxides and silicates) with heat sinks such as carbonates and hydroxides.

8.6 Titanates

Potassium titanates have eventually entered into formulations in the so-called “non asbestos organic” (NAO) materials, currently without steel fibers, because they offered an alternative fiber-like material to replace asbestos, in order to provide a suitable framework for friction materials. Potassium titanates have a high melting point of around 1300 °C. Moreover, their friction stability and gentle behavior for both wear and noise were surely added values. Among several other whisker materials, potassium titanates provide a low material wear. Their introduction caused a considerable shift from metallic formulations towards ceramic (NAO) ones. However, the potassium titanate whiskers are in the size range of respirable fibers, and they are suspected to be carcinogenic as reported by the European Chemical Agency in the form of hexatitanate.

The potassium titanates are usually classified on the basis of the molar ratio between the formal content of TiO_2 and K_2O . The general formula of potassium titanates can be written as $\text{K}_2\text{O} \cdot n\text{TiO}_2$ with n being the variable. The most utilized phases are the hexatitanate $\text{K}_2\text{O} \cdot 6\text{TiO}_2$ and the octatitanate $\text{K}_2\text{O} \cdot 8\text{TiO}_2$, while the “monotitanate” $\text{K}_2\text{O} \cdot \text{TiO}_2$ is almost never used in this field. Depending on the impurities or dopants, which may alter the growth of the crystal, the material can be more or less fibrous. [Figure 8.11](#) shows particles of a potassium hexatitanate with a low content of free whiskers.

The structure of potassium hexatitanate is monoclinic ($a=15.58 \text{ \AA}$, $b=3.82 \text{ \AA}$, $c=9.11 \text{ \AA}$, $\beta=99.76^\circ$) and each cell contains $2(\text{K}_2\text{Ti}_6\text{O}_{13})$, while the basic units are TiO_6 octahedra with shared oxygen with other Ti atoms as in rutile (TiO_2). However, the presence of the large K^+ ions causes a different arrangement in the a - and c -direction, restraining the octahedral packing [10]. In this regard, see [Figure 8.12](#), which shows a projection of the atoms' arrangement with TiO_6 octahedra and K^+ ions on the a - c plane. The introduction of small amounts (around 2 wt.%) of alkaline earth metals in the synthesis process such as Ca^{2+} and Mg^{2+} , or alkali metals such as Li^+ and Na^+ , which all have a smaller ionic radius than K^+ , may reduce the fibrous aspect of particles while preserving the same crystalline phase.

On the other hand, the potassium and magnesium titanate $\text{K}_2\text{O} \cdot \text{MgO} \cdot 4\text{TiO}_2$, which has a platelet shape, has not found a wide application in substitution for the hexatitanate, possibly because, due to the platy shape, no added value is delivered in comparison with potassium titanates with $n > 4$.

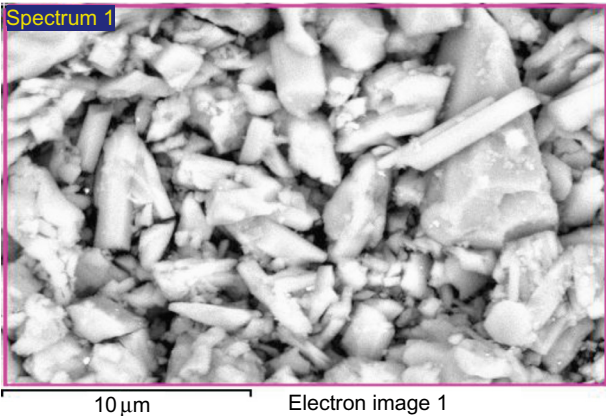


Figure 8.11 Potassium titanate (hexatitanate) with a low content of whiskers.

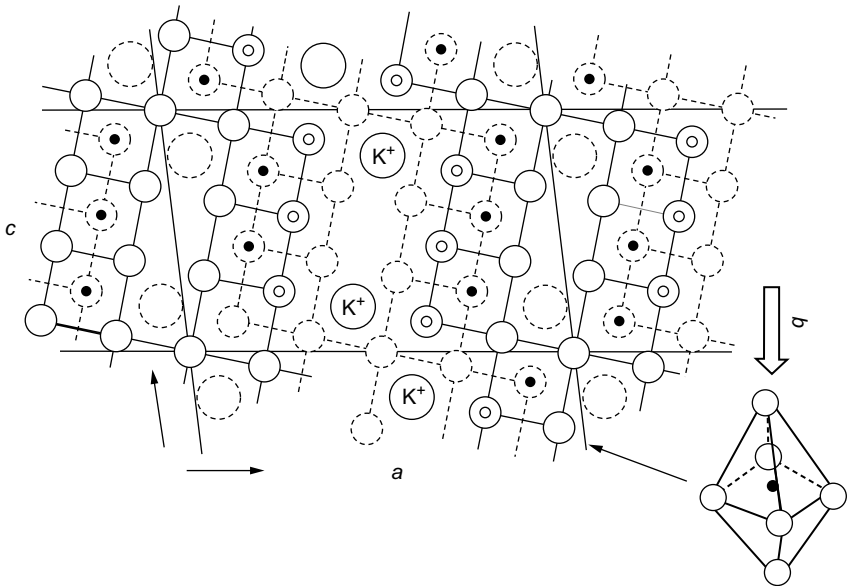


Figure 8.12 Projection of the potassium hexatitanate on the *a*–*c* plane. A TiO₆ octahedra is shown on the right side [11].

8.7 Silicon carbide

Silicon carbide, also known as *carborundum* for analogy with the aforementioned *corundum*, has to be mentioned because it is the nearly nonoxygen ceramic used in friction materials, and is often used in small amounts (0.2–0.5 wt.%) as a strong abrasive as an alternative to corundum together with zircon sand. Although both C and Si

are sp^3 hybridized, it is noteworthy to point out that silicon carbide is polymorphic, α - and β -SiC being the most common polytypes with hexagonal and cubic (zinc blende) structures, respectively. In friction materials, the most common phase is α -SiC and the black color is from the iron impurities. An SiO_2 film always covers the surface decreasing the abrasive effect, the coefficient of friction, and the heat transfer. The thermal conductivity of silicon carbide is relatively high, between 250 and $50 \text{ W m}^{-1} \text{ K}^{-1}$, depending on temperature and the oxide film growth. Although its high thermal stability of up to 2700°C , at which it sublimates in inert atmosphere, in air oxidation becomes severe from 1400°C , forming the less abrasive SiO_2 as well as hydroxylated silica (i.e., silicic acid) as indicated in Equations (8.4) and (8.5).



Even though such high temperatures are not achieved in friction contacts, the oxidation reaction can be enhanced by friction through a tribochemical pathway that decreases the energy barrier and consequently the actual temperature to speed up the reaction. The reaction of Equation (8.5) may cause a tribochemical wear due to friction for the removal of silicic acid or short silica polymers such as $(HO)_mSi_p(SiO_2)_n$. The ionic potential of oxides has proven to be an interesting parameter in correlation with the adhesion forces of these soft oxides and consequently with the coefficient of friction. High ionic potentials usually correspond to low friction, and Si^{4+} ionic potential is quite high, around 10, thus providing a low coefficient of friction considering that these oxides slide against an oxidized metallic film [11]. This ambivalent behavior of both abrasive and lubricant material made SiC an ideal candidate for the basic ceramic rotor matrix.

8.8 Clays and aluminosilicates

Although the carcinogenic asbestos belongs to this general family, there are many other aluminosilicates or clays that are not fibrous, or are without respirable fibers. Moreover, it should be noticed that the pathogenicity of silicates is also linked to active sites and not only to the fibrous nature. Examples of clay formulas are kaolinite $2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$, pyrophyllite $4SiO_2 \cdot Al_2O_3 \cdot H_2O$, talc $4SiO_2 \cdot 3MgO \cdot H_2O$, and chamosite $3SiO_2 \cdot Al_2O_3 \cdot 5FeO \cdot 4H_2O$. The SiO_2 ratio in a formula is the key factor determining clay mineral types. These minerals can be classified on the basis of variations of chemical composition and atomic structure into different groups: (a) kaolin–serpentine (kaolinite, halloysite, lizardite, chrysotile), (b) pyrophyllite–talc, (c) mica (illite, glauconite, celadonite), (d) vermiculite, (e) smectite (montmorillonite, nontronite, saponite), (f) chlorite (sudaite, clinocllore, chamosite), (g) sepiolite–palygorskite, (h) interstratified clay minerals (e.g., rectorite, corrensite, tosudite), and (i) allophane–imogolite.

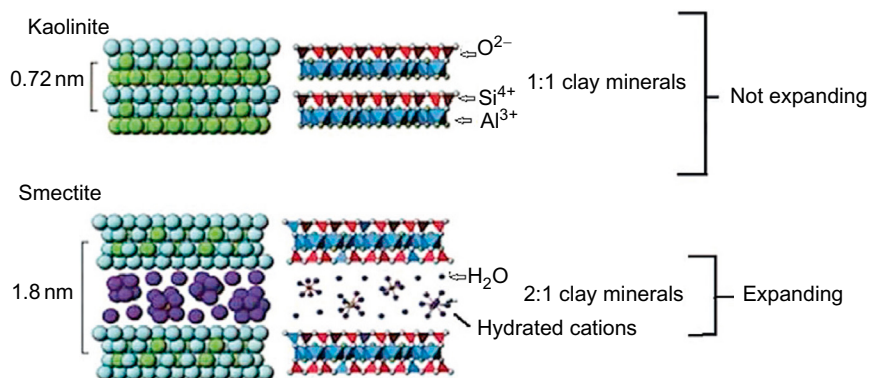


Figure 8.13 Kaolinite and smectite sandwich structures as an example of different properties of clays.

The basic structure of clays is alternating lamellae made of SiO_4 tetrahedra and AlO_6 octahedra. The ability to expand is due to the filling of the alternating lamellae by a considerable amount of water and cations. A schematic example of two types of clays is depicted in Figure 8.13, where kaolinite and smectite basic sandwich structures are shown with the interlamellar space, which confers different properties (i.e., expansion or nonexpansion).

The main characteristics of clays are the elevated surface areas around $30 \text{ m}^2 \text{ g}^{-1}$ for kaolinite, $60\text{--}80 \text{ m}^2 \text{ g}^{-1}$ for halloysite, and above $600 \text{ m}^2 \text{ g}^{-1}$ for montmorillonite. Concerning friction materials, the most remarkable characteristics of clays are expansions, de-oxydriation water loss above 400°C , low size of particles (agglomerates can achieve a size of $45 \mu\text{m}$ but are composed of many small particles very often below $5 \mu\text{m}$) that makes them suitable as fillers, “soft abrasives,” thermal insulators, reinforcing agents in materials with high content of resins, and heat sink. Thermal gravimetric analysis and differential scanning calorimetry (DSC) results show that clays occupy an intermediate position between alkaline earth metal hydroxides, such as $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$, and carbonates as a heat sink with endothermic de-oxydriation peak temperatures between 500 and 700°C , as shown for the kaolin group in Figure 8.14 [12]. The endothermic peaks of some types of kaolin clays are shown, and the chrysotile asbestos DSC curve has been included for comparison. It is noteworthy to point out that the de-oxydriation temperatures which are included between 500 and 700°C can vary depending on the mineral site, since clays of the same class can have composition and morphology differences depending on the mine site. Kaolinite and halloysite seem to be the best heat sinks of this group. At higher temperatures, above 800°C , the exothermic peak corresponds to the crystallization heat of γ -alumina from the destroyed clay structure.

Clays are very suitable for the “underlayers,” used as a layer of material blend interposed between the back-plate and the proper friction material, which is used to improve adhesion and the thermal barrier with a variable thickness around 3 mm . The low cost of clays allows a decrease in the total cost of these underlayers.

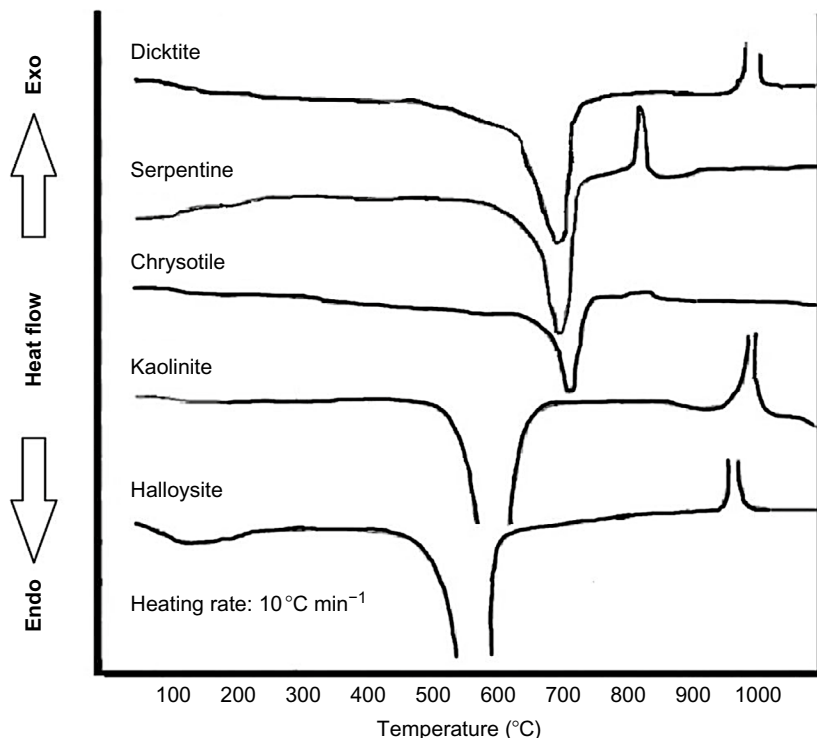


Figure 8.14 Differential scanning calorimetry curves for the kaolin group of clays.

R.C. Mielenz, N.C. Schieltz, M.E. King, Thermogravimetric Analysis of Clay and Clay-Like Minerals, University of Missouri, Columbia, MO, October 15–17, 1953, pp. 285–314.

8.9 Barium sulfate: Barite

A special mention must be given to barite, i.e., a mineral composed of BaSO_4 , which is the most common filler with a high density of 4.48 g cm^{-3} , used in friction materials both for the high density, which allows compounders to utilize low volumes, and low costs. Low volumes mean a low effect on friction in comparison to large volumes, i.e., low densities. The low Mohs hardness (3–3.5) also has contributed to its use since it is generally considered to be an inert material from the friction point of view. Most studies use barite to compensate for the variation of other components to keep the total mass fraction equal to 1; however, the effects determined are very often affected as well as by the change of barite mass fraction. It was found that a balance of barite and metals may control excessive pad wear.

8.10 Abrasive wear

8.10.1 Hardness effect

Abrasives are the hardest materials in friction compounds and they are the least deformable both elastically and plastically, so that under the pressure and stress of

friction they strain and ultimately remove worn material from the contact surface. For these reasons, hardness, shape, and size are determinants of wear in spite of composition, microstructure, and structure. Bond strength, microstructure, and structure determine the way in which abrasives, which are brittle materials, are broken and fractured in, or may deform, a countersurface. On the other hand, shape and size in particular determine the way contact surfaces are worn by abrasives and consequently affect the useful life of both the friction material and the rotor.

The ratio between the particle hardness H_p and the hardness of a flat surface H_s determines the possibility of plastic scratch. The threshold value of $H_a/H_s > 1.2$ has been found with several methods, including the slip-line field theory. Abrasion occurring at values of H_a/H_s higher than 1.2 is called hard abrasion, while that occurring at lower values is often called *soft abrasion*, for example that which may be caused by calcite. The ratio H_a/H_s for the couple of alumina and gray cast iron, as an example, is around 7, far above 1.2, while that of the couple calcite and gray cast iron is around 0.6, leading to soft abrasion as stated, until the decomposition of calcium carbonate begins.

Another characteristic of abrasives is that they are subject to fracture, since they are brittle and may cause fracture on the surface and consequently wear, so that the original shape and size of abrasive particles can change, especially during three-body wear, where collisions between hard particles are very probable. Therefore, estimation of size and shape effects may be changed during friction. Ceramic and glass fibers, which are used to provide an armor-like structure, are finely cracked in three-body friction.

8.10.2 Shape and size effects

Angular particles cause higher wear than round-shaped particles. A simple description of a shape factor is obtained through a two-dimensional projection of the particle as generated in an optical microscope. A roundness factor can be defined as the ratio between the projected area and the area of the circle with the same perimeter p as in the projection:

$$F = \frac{4\pi A}{p} \quad (8.6)$$

$F=1$ means that the particle is circular, and the lower the F values are, the more the particle will depart from a circle. The average of F values of many particles randomly oriented will provide a value of the shape of 3D particles with respect to a sphere. It is noteworthy to point out that three-body wear can be milder than two-body because the particles rolling offer a lower attack angle to the surface.

The attack angle θ_a is a criterion used to determine the possibility of wear due to abrasive particle cutting. It is important to mention that the attack of abrasive particles can give origin essentially to three modes of abrasive plastic deformation in order of increasing θ_a : plowing, wedging, cutting, where the last two lead to wear [13]. The controlling factors are the previously mentioned attack angle and the shear strength of the interface between the hard particle and the surface. This can be expressed by means of the ratio f between the shear stress at the interface and the shear yield stress of the plastically deforming material. Thus $f=0$ is the case of perfect lubrication, $f=1$

perfect adhesion, and for $f < 0.5$ only two modes of deformation are possible: plowing and cutting. For $f > 0.5$ all three modes can occur, passing from one to the other depending on the attack angle.

The size effect can be understood by reasoning on spherical abrasive particles in two-body friction against a flat surface, for example. Taking the Archard wear law as elaborated in Chapter 2, the specific wear rate K of Equation (2.29) is not only a function of temperature, in its form expressed as volume worn per energy unit:

$$K = \frac{V}{E} \quad (8.7)$$

the volume V is correlated to abrasive particle size, since V is proportional to the applied load F_N , according to the Archard law. Moreover, F_N is in turn proportional to $d^{1/2}$ for contact spherical particles for two-body wear against a flat surface, so that

$$K = \frac{cd^{1/2}}{E} \quad (8.8)$$

where c is a parameter that depends on the elastic modulus, the number of contact particles, shear strength of the tribofilm, etc.

A consequence of Equation (8.6), is that, if K is quite constant, although V is lowered by small particles, the energy dissipated E is also lowered and this might decrease the coefficient of friction μ , according to the fact that μ is proportional to the energy dissipated E , i.e., the work dissipated of Equation (1.3). This is in accordance with the general idea that abrasives may increment the coefficient of friction. However, this effect may be either mitigated or compensated by other effects, which increment the dissipated energy through other mechanisms. It is noteworthy as a reminder to mention that the friction materials are composites and the rotor is metallic, so that adhesion forces between tribofilms may compensate for the energy not dissipated by abrasion and deformation.

8.11 Nanopowders

In the last few years, the newly developed technologies, whether products produced at industrial scale or separated nanoparticles from coarser mineral powders, have opened the door for friction compounders to have at their disposal raw materials that in theory can drastically reduce wear and exhibit different friction performance from their coarser counterparts. The case of nanominerals is very interesting for their lower cost in comparison with synthetic products; for example, nanoclays such as halloysite, containing nano- and microtubules, are gaining large support for applications in composites. A study presented by Bijwe et al. [14] reported a comparison between the effect of three nanoabrasives: nanoalumina, nanosilicon carbide, and nanosilica, all compared with their corresponding coarser products.

The tribometric test results on wear are quite in favor of the theory exposed in Section 8.10.2, which states that large effects will be found at the very small sizes due to the power $1/2$ on the diameter d of Equation (8.6). In this study a simplified composite

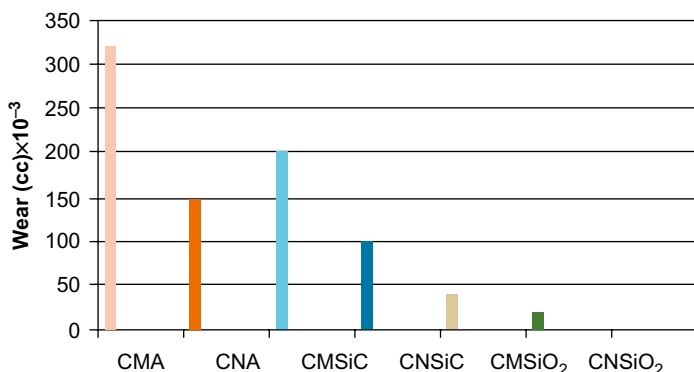


Figure 8.15 Wear of composites with 2 wt.% of CMA (microalumina), CAN (nanoalumina), CMSiC (micro-SiC), CNSiC (nano-SiC), CMSiO₂ (micro-SiO₂), CNSiO₂ [12].

matrix was used without steel fibers varying the 2 wt.% of abrasives of different type and size from micro- to nanoscale. The effects on material wear for CMA (microalumina, size 48–100 μm), CNA (nanoalumina, size 40–80 nm), CMSiC (micro-silicon carbide, size 3–110 μm), CNSiC (nanosilicon carbide, size 50–60 nm), CMSiO₂ (microsilica, size 3 μm), CNSiO₂ (nanosilica, size 15 nm) are reported in Figure 8.15. The smaller sizes considerably reduce wear, in some cases up to 50% in the reported tests, executed with pressures between 1 and 4 MPa, speeds between 600 and 1200 rpm, and 125 braking applications at the initial temperature $<80^\circ\text{C}$. However, it should be taken into account that the size effects are superimposed on the shape ones.

The speed and pressure sensitivities of this test, carried out with a tribometer using a pad sample and real rotor, can only give an indication of what may happen in situations closer to applications. Nanoabrasive powders led to higher coefficients of friction than micropowders, and the variation of the average coefficient of friction was less compared to the materials with the micropowders. Moreover, nanoabrasives performed better under severe sliding conditions rather than in mild conditions. Load-speed sensitivity was in general lower for nanoabrasives. This beneficial effect may be attributed to more stable, thin and coherent tribofilms on both pad and rotor surfaces.

However, the big challenge with nanomaterials, in spite of their performance, is related to handling and blending for health issues. Since they have a large surface area they tend to form micro-agglomerations held together by electrostatic forces, which must be broken to improve their mixing, making the dispersion in the matrix difficult.

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9.1 Introduction

Metal content in friction materials can vary from 5 to 50 wt.%. Currently, the content of metals is decreasing for many reasons, including prices of certain metals and noise concerns. Their main benefits are related to heat removal from the friction interface and the contribution to the composite film, which is present on both the friction material surface and the rotor one. The most thermally conductive metal used in friction is copper; nevertheless, restrictions and banning rules in the United States are pushing towards copper-free materials. This fact has caused a steel fiber revival, after the decline in the past decade due to the advent of steel-free materials. However, the content of carbon of newly developed steel fibers is usually below 0.1%; moreover, these new fibers are also often annealed to decrease wear and noise effects.

Heat removal has a significant effect on the preservation of the binder, reducing the consequent oxidative wear. Metallic fibers such as steel fibers contribute considerably to the material strength, and are much less expensive than organic fibers, with the exception of cellulose which contributes only to preforming, before hot molding, and poorly to final material reinforcement.

From the tribological point of view, metal–metal contacts exhibit a high coefficient of friction (more than 0.4), due to their high adhesive forces, but in air this contact is evanescent since surface oxides are rapidly formed. This explains why the combination of metals and abrasive is a key factor in controlling the stability of the coefficient of friction, avoiding peaks and fading of friction. Sulfides are mediators in this process of alternative high coefficients of friction (metals on metals) and lower ones (oxides on oxides). If not tempered by sulfides and lubricants, this situation can lead to brake-torque variation and consequently to either noise or vibrations. Metals such as Cu, Zn, Sn and Cu alloys are generally very expensive and price fluctuations are common, and the current trend is a decrease in their use. For instance, Zn (and Sn to a certain extent) was mainly used as sacrificial element to prevent rust formation in the interface between pad and rotor, which ultimately causes sticking after parking. Nowadays, this phenomenon is handled in another way by creating an alkaline environment less inclined to oxidation with the addition of small amounts of Ca(OH)_2 to the friction material blend. Summing up, metals are fundamental components for both heat removal and reaching an adequate coefficient of friction, without forgetting that the balance of all the main components—metals, abrasives, lubricants, and sulfides—is the key to obtaining a steady coefficient of friction.

9.2 Steel fibers and iron powders

Steel fibers have continuously been present in friction material, although they had a decline in the first decade of the twenty-first century. However, the banning of copper in car brake pads in certain states in the United States (virtually causing it to no longer be used throughout the country) has started a revival of steel fibers. As said, steel fibers are involved in the noise process. Their revival is linked to their substitution for Cu, to contribute to thermal conductivity. Nevertheless, this process required a rethinking of steel fiber processing: i.e., the content of carbon must be lowered and the annealing processes to release stresses must be considered as well. For instance, several companies already offer steel fibers with less than 0.10% carbon to decrease noise problems. Steel fibers as metallic compounds are also involved in the stability of friction and in the thermal conductivity of the brake pad composite. The main effects of thermal conductivity on friction material performances concern severe conditions such as fading and recovery. In this case, a high temperature is reached through repeated braking applications as in a downhill stress and recovery; the material must be able to restore the steady coefficient of friction after cooling. A study conducted by Bijwe and Kumar [1] in a Krauss machine was not conclusive, at least for steel fiber contents, till 12 wt.% in a model matrix. However, they showed that fading and recovery is better for the material with the 12 wt.% steel fibers. These studies, where the formula balance is achieved by adjusting barite content, always have the limitation that the effect of the raw materials varied can be exchanged, since the supposed friction inertness of barite is still to be demonstrated, especially for formulas with mild abrasives and low metallic content. Nevertheless, the improvement of fade behavior by means of using a low content of steel fibers (around 10 wt.%) should not be neglected, because it can make the difference in many applications where the metal content must be strictly controlled or reduced. In the Bijwe study, the thermal conductivities of the materials with steel fibers from 4 to 12 wt.% were 2.39 and 2.51 W m⁻¹ K⁻¹, respectively, i.e., 0.015 W m⁻¹ K⁻¹ for each percent of steel fiber, so the contribution seems to be too small to be a suitable substitute for copper. Also, diffusivity does not seem to be considerably increased. Another study by Kumar et al. tried to compare some metallic raw materials such as steel fibers, brass fibers, and copper powder in a non-asbestos organic matrix. Although the different morphology of the raw materials was not taken into account, the values for thermal conductivity show the significant effect of copper is not achieved by steel fibers, even with 20 wt.% [2]. Some effect on speed sensitivity, including steel fibers, was found for the highest amount studied. In any case, metals seem to assure better friction stability in the materials. No direct benefit was found on the material wear due to metals. However, steel fibers provide a better behavior, as was already shown in Figure 3.5.

Iron powders are common in both semimetallic formulations as well as in low metal ones. As with any metal, they contribute to the level of friction; this effect is even more important in current materials with few and mild abrasives. Their usual round-shaped form and low carbon makes them less aggressive towards the rotor surface. Moreover, the sponge iron powder is less noisy than bulk iron powder and is a reasonable alternative to steel fiber to achieve the desired level of iron in the formula (Figure 9.1) [3]. A technical report by Hu clearly indicated that friction material with

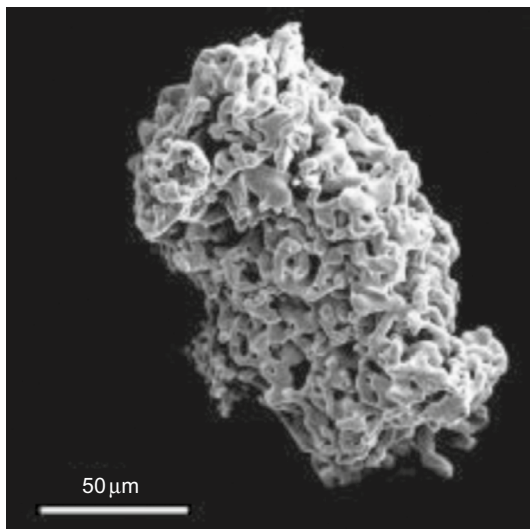


Figure 9.1 Sponge iron from H_2 reduction.

sponge iron, which is softer and has a large surface area and a low particle density between 6.48 and 6.74 g cm^{-3} (remember that bulk iron density is 7.87 g cm^{-3}), caused less noisy braking applications in the test SAEJ2521. Hu kept the semimetallic formula ingredients constant and varied only the type of iron powder: sponge H_2 -reduced, carbon reduced, and water atomized.

The hardest water-atomized iron powder gave the worst noise, with an additional frequency at 12 kHz . These study results are due to a combination of properties of the H_2 reduced sponge iron: high porosity and low hardness. Porosity favors noise dissipation and low hardness lowers the coefficient of friction, which in turn reduces the intensity of noise and can even decrease the instability of the coefficient of friction so that the probability to excite a certain resonance frequency also decreases, as in the case of low hardness.

9.3 Copper and copper alloys

As is known, copper is one of the most thermally conductive materials (around $400 \text{ W m}^{-1} \text{ K}^{-1}$), only overtaken by silver among metals, and its use is mainly related to heat dissipation on the contact surface. Moreover, copper, like other metals, contributes to the coefficient of friction increasing when direct contact is provided, as well as to the composite oxide film on the disk surface.

The particle size acquires a fundamental importance in metals because, depending on size, the metal particles can be more easily strained and oxidized. For example, it is known that metal nanoparticles melt at temperatures considerably below the bulk melting temperature.

Experiments carried out with gold particles showed that below 10 nm the melting point decreases dramatically; a similar effect can also be expected for Cu, which belongs

to the same group as Au [4]. In this case, at 20 nm the melting point is around 1300 K, i.e., the bulk melting temperature, while at 5 nm it is around 1000 K, 300 K less!

As the size of a particle decreases, the surface-to-volume ratio is inversely increased proportionally with respect to the radius of the particle. As a result, the surface atoms become prone to detach from their positions and diffuse on the surface. Surface diffusion is followed by a partial melting of the nanoparticle, mainly within a thin layer close to the surface, which is called *surface melting* or *premelting*. The surface melting generally occurs at temperatures much lower than the bulk melting, but the details depend on the parameters such as size, morphology, defects, strain, and of course crystallographic orientation of the surface.

A similar study carried out on spherical copper particles embedded in a silica matrix by Yeshchenko et al. [5] showed that the melting temperature T_m decreases from 835 to 450 °C from a diameter of 62–35 nm (see Figure 9.2). It is noteworthy to point out that the bulk copper melting temperature is 1084 °C and the considerable decreasing of the melting temperature with decreasing size particles can explain a certain lubricant effect due to copper and copper alloys, and other soft metals. Small metallic particles can thus form films protecting the rotor, and increasing contact area. Copper and its alloys may be responsible for speed sensitivity when not adequately balanced with sulfides.

It is easy to understand that either Zn or Sn particles can act in this way as well as copper alloys, such as bronze and brass. However, bronze and brass are being used much less in the last few years, and often their use is connected more to an esthetic purpose rather than a real contribution. Only brass chips and copper fibers may contribute

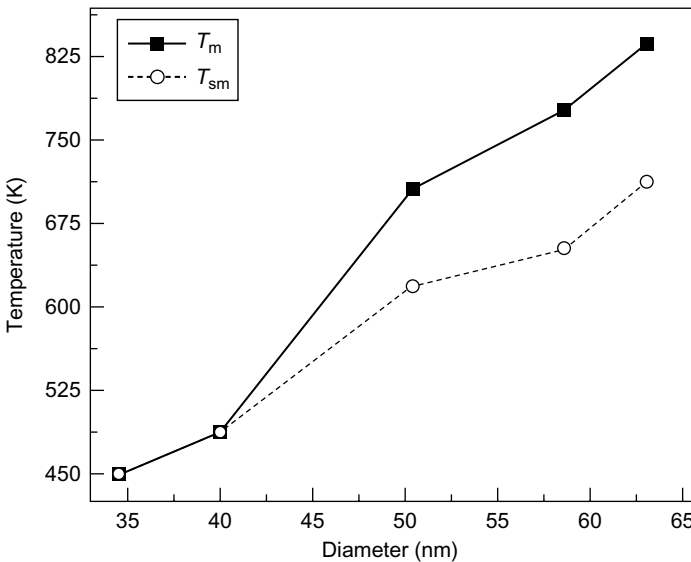


Figure 9.2 Dependence of melting temperatures (T_m : melting temperature, T_{sm} : surface melting temperature) and surface melting of copper nanoparticles on their diameter.

O.A. Yeshchenko, I.M. Dmitruk, A.A. Alexeenko, A.M. Dmytruk, *Size-dependent melting of spherical copper nanoparticles embedded in a silica matrix*, *Phys. Rev. B* 75 (2007) 085434.

to a certain extent to reinforce structure, as with steel fibers. In the work by Sharma et al. [6] the effect of copper on both thermal conductivity and diffusivity in friction materials is analyzed; however, thermal effusivity is not considered. Graphite exhibits a considerably high thermal diffusivity ($\sim 1000 \text{ mm}^2 \text{ s}^{-1}$) along the plane and its thermal conductivity ($\sim 100 \text{ W m}^{-1} \text{ K}^{-1}$ at 400 K), also along the plane, is much lower than that of copper and drops considerably with temperature. For these reasons, anisotropy and a relatively lower thermal conductivity, graphite is not a clear adequate substitute for either copper or any other metal in friction materials.

The work by Sharma et al. [6] showed that the introduction of a small amount of Cu nanoparticles (2 wt.%, 50–200 nm) instead of coarser particles (400–600 μm) not only increased both thermal conductivity and diffusivity but also provided a better speed sensitivity, fade, and wear. These friction performance improvements are possibly linked to the melting temperature lowering effect of smaller particles.

9.4 Thermal diffusivity and other thermal properties

Thermal diffusivity is a parameter to be taken into account; however, a high value does not necessarily mean that heat is better dissipated, since it is the ratio between the thermal conductivity and the volumetric heat capacity at constant pressure. It provides information about the competition between heat conduction and storing, and both can be useful to keep temperature as low as possible:

$$a = \frac{\lambda}{\rho C_p} \quad (9.1)$$

where in Equation (9.1), a is the thermal diffusivity, λ is the thermal conductivity, ρ is density, and C_p is the heat capacity. Temperature governs the speed of chemical reactions and flash temperature contributes to the rate of tribochemical reactions too. Thermal diffusivity of a material is related to the speed to reach thermal equilibrium under variable thermal conditions. For this reason, low values are better, to reduce the possibility that a high temperature can be reached in depth and damage the binder deeply. The thermal diffusivity says nothing about the energy flows. On the other hand, the thermal effusivity characterizes the ability to exchange thermal energy with its surroundings. Thermal effusivity is given by the following equation:

$$e = \sqrt{\lambda \rho C_p} \quad (9.2)$$

In summary, thermal effusivity and diffusivity are representative of two phenomena in competition: the former is related to the ability of the material to absorb heat, while the latter to the speed to reach thermal equilibrium, i.e., to adapt itself to the surroundings. Thermal effusivity explains, for example, why at touch metals seem colder than other bodies at the same temperature, since the heat transfer from the skin to the metal is very fast. In other words, diffusivity is related to heat penetration and effusivity to surface heat exchange. During friction a lot of heat is created at the interface, and this heat must be dissipated; thus the most effective friction material is that which can

Table 9.1 Thermal diffusivity (a) and thermal effusivity (e) of some engineering materials at room temperature

Material	a (mm ² s ⁻¹)	e (W cm ⁻² K ⁻¹ s ^{-0.5})
Fe	20.4	1.59
Cu	115	3.69
Al	91	2.37
Al ₂ O ₃	10.5	0.56
SiO ₂	0.85	0.15
Polycrystalline graphite	100–60	1–0.7

absorb (dissipate) more heat without raising temperature. Therefore, thermal effusivity (a surface property) seems to be more important than thermal diffusivity (a bulk property). In Table 9.1 a list of thermal diffusivity and thermal effusivity values of some materials is reported.

Table 9.1 shows that the handicap of graphite is plane orientation, which reduces the effect of the high in-plane conductivity, leading to a very low thermal effusivity and a medium thermal conductivity. To a certain extent Fe can have a greater effect. However, this effect could be considerably reduced with graphite with low L_c approaching the graphene layer and extended plane development. This strategy may offer an alternative to the massive use of metals. The reduced L_c is really always achieved in the friction interface, since graphite layers slip and are separated. Therefore, we can say that L_a (i.e., the in-plane extension of crystallites) or, even better, the ratio L_a/L_c is really the fundamental parameter controlling high thermal effusivity of graphite.

9.5 Friction of metals in air

Apart from being large contributors to heat dissipation, metals, due to the characteristics of the metallic bond, contribute considerably to the coefficient of friction, since the friction mating of two metals is highly probable in brakes due to the rotor and the metallic components of friction materials. However, the coefficient of friction of metals depends on the presence of oxide layers (which cannot be avoided in air), the type of metal, its microstructure, and the type of alloy. For example, alloys usually exhibit a lower coefficient of friction. Even the oxide layer type has its influence when there is polymorphism, or when the metal can acquire different states of oxidation. At the contact surface, the adhesion force F_{adh} , which is one of the major contributors to the friction force, is linked to the asperity junction between and the shear strength:

$$F_{adh} = As \quad (9.3)$$

where A is the asperity contact area and s the shear strength of the adhesive contact.

Therefore, the adhesive component is given by:

$$\mu_{adh} = \frac{As}{W} \quad (9.4)$$

In addition, the deformation component μ_{def} is given by:

$$\mu_{\text{def}} = \cot \alpha \quad (9.5)$$

where α is the semi-angle of a conic asperity. Highly ductile metals such as Sn, Cu, etc. will be deformed very easily so that the angle α will be 90° and the μ_{def} contribution will be very low or even null. In any case, a variable oxide film will always cover any metal that is rubbing in air, so the metal coefficient of friction becomes:

$$\mu = \frac{F_{\text{max}}}{W} = \frac{1}{2[(\tau_0 / \tau_i) - 1]^{1/2}} \quad (9.6)$$

where F_{max} is the tangential force achieved at the maximum contact area A_{max} , τ_0 is the bulk material shear strength, and τ_i the oxide film shear strength. Since oxides exhibit a low coefficient of friction, when the pure metal surface is exposed due to abrasion or delamination, the coefficient of friction should rise to infinitum according to Equation (9.6). However, air and humidity prevent pure metal surfaces from being exposed for a long time, since a thin oxide layer is always rapidly formed, especially under friction. Nevertheless, we can attribute to metals an increase in the coefficient of friction when playing together with abrasives, which remove the oxide film from the metal surface. This ambivalent behavior due to the oxide film and pure metal exposure is probably one of the main sources of noise and vibration problems concerning the fluctuation of the friction force, due to the continuous alternation between an oxide film and pure metal.

Therefore, the content of abrasives is more related to that of metals than lubricants. On the contrary, lubricants act as mediators between abrasives and metals, interposing a film that prevents an excessively high coefficient of friction due to the exposure of the pure metal surface, and preventing a too-rapid oxidation through a sacrificial oxidation. This possible behavior is summarized in the sketch of Figure 9.3.

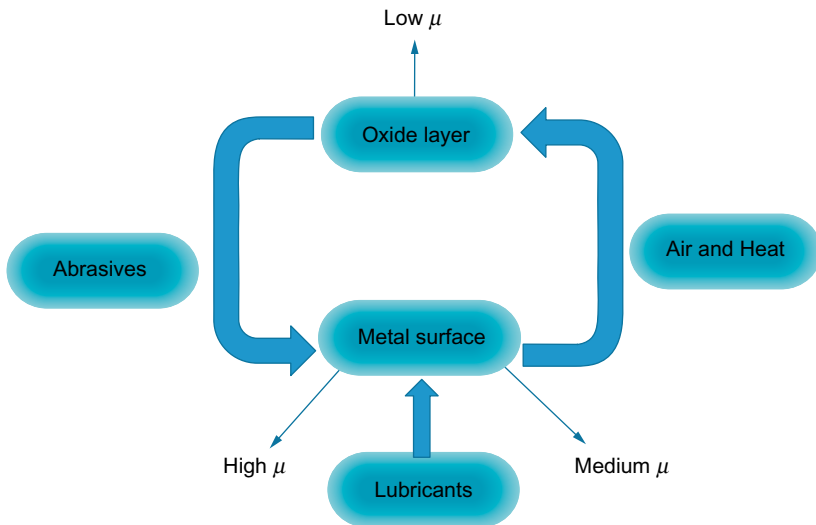


Figure 9.3 Cycle of metals in friction materials.

9.5.1 Metal transfer

The main characteristic of metals is the ability to be transformed and transferred from the friction material surface to the rotor surface and back. The process begins when the metal particle emerges on the surface. At this stage it is strained by the shear stress increasing the contact area, as already described. In Figure 9.4 the strain on the surface of a steel fiber is shown in a cross-section optical micrograph of a friction material that underwent a performance dynotest [7].

Metal is not only transferred due to a combination of shear stress and adhesion, but it is also chemically transformed to oxide and becomes part of a composite layer that is eventually removed, forming wear debris, which can be plastically deformed and become part of the friction layer again. Tests carried out on a semimetallic material with 4 wt.% of Cu showed the presence of Cu_2O on the friction layer after a dynotest together with FeO, which is of course the dominant component. A transmission electron microscope (TEM) image showed the nanometric texture of this layer where metal oxide particles are included in the FeO composite matrix (see Figure 9.5).

The effect of the formation of the oxide layer is more evident in metal matrix composites (MMC) as in the case of metallic sintered friction materials; also the effect of graphite as a friction modifier is even more evident in this case. Too-low lubricant contents in a metallic matrix may cause a higher coefficient of friction at low loads, and consequently a load sensitivity, which is never appreciated. Gultekin et al. carried out tribological experiments with a Cu-MMC containing a variable amount of polycrystalline graphite with an average size of $80\text{ }\mu\text{m}$ [8]. Five Cu-MMC pads were prepared with 1, 2, 3, 4, and 5 wt.% of graphite, and rubbed against an Al-MMC (Al–Si–SiCp MMC) disk. The material with the 4% graphite exhibited the best friction stability and the lowest load (pressure) sensitivity. Moreover, the material with 5 wt.% of graphite performed worse than that with 4 wt.%, possibly due to the poor strength of the composite. The presence of Cu oxides was detected on both surfaces, indicating a significant transfer from pad to disk; on the other hand, SiC particles



Figure 9.4 Section perpendicular to friction surface showing the considerably plastically deformed steel chip marked with an arrow.

J. Kukutschová, V. Roubíček, K. Malachová, Z. Pavlíčková, R. Holuša, V. Míčka, J. Kubacková, D. MacCrimmon, P. Filip, Wear mechanism in automotive brake materials, wear debris and its potential environmental impact, Wear 267 (2009) 807–817.

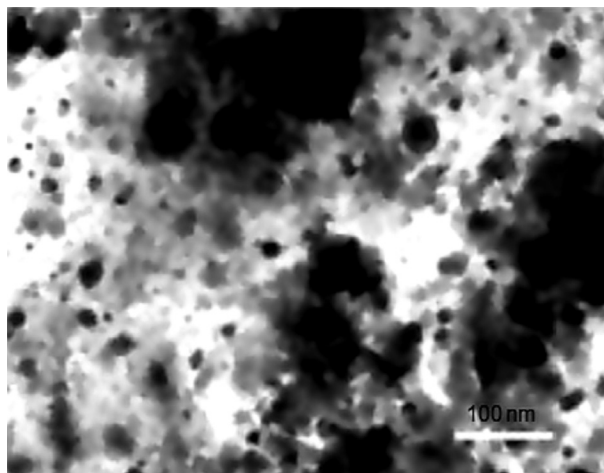


Figure 9.5 TEM bright field showing microstructure of the friction layer.

J. Kukutschová, V. Roubíček, K. Malachová, Z. Pavlíčková, R. Holuša, V. Míčka, J. Kubacková, D. MacCrimmon, P. Filip, Wear mechanism in automotive brake materials, wear debris and its potential environmental impact, Wear 267 (2009) 807–817.

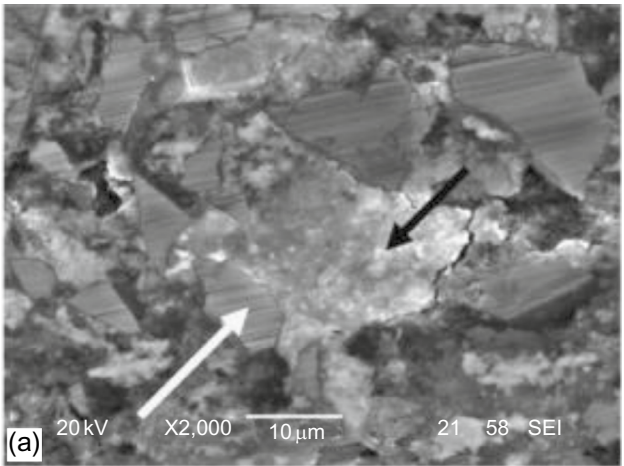
were found embedded in the pad surface layer. In summary, there is a net transfer of abrasive particles and Al from disk to pad, compensated for by a net transfer of Cu from pad to disk, presumably both through a third-body stage. It is also interesting to observe the presence of a graphite transfer to the disk surface, which prevented a too-rapid metal oxidation.

It is noteworthy to observe that Al and Cu seemed to be part of a composite oxide film as shown in [Figure 9.6](#).

In other words, graphite not only forms an interposing layer that reduces metal–metal direct contact, but also prevents oxidation possibly through a sacrificial oxidation and as a protective barrier becoming part of the composite layer.

In this study, the wear mechanism changed from the main abrasive one, characterized by plowing and cutting, at low loads (2–5 N), to a predominant delamination wear at higher loads (10–20 N), which caused a detachment of the composite film (mainly copper and aluminum oxides). This severe wear is really related to oxidative wear, which is typical of metals, and is a form of fatigue wear. This phenomenon is well illustrated in [Figure 9.7](#).

Another issue that is almost neglected is that of airborne particles, especially those produced by train brakes, which are mostly originated from the metals contained in both rotor and friction material. Most particles are in the nanosize range from 100 to 600 nm [9]; however, the size spectrum goes up to microsize, but still very fine particles that have a health and environmental impact. These represent the true wear particles, since they got out of the cycle of the composite oxide layer formation.



Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic (%)	Cone	Units	
C	Ka	4.02	1.268	29.973	13.213	wt.%	
O	Ka	38.15	3.905	37.948	22.284	wt.%	
Al	Ka	20.14	2.837	3.543	3.509	wt.%	
Si	Ka	30.62	3.498	4.273	4.404	wt.%	
Cu	Ka	141.10	7.510	24.263	56.590	wt.%	
				100.000	100.000	wt.%	Total

(b)

Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic (%)	Cone	Units	
C	Ka	9.32	1.930	69.344	49.170	wt.%	
Si	Ka	856.15	18.501	30.656	50.830	wt.%	
				100.000	100.000	wt.%	Total

(c)

Figure 9.6 (a) SEM micrograph and EDS analysis of disk surface that illustrates the presence of transfer layers, (b) points at black arrow, and (c) points at white arrow at 10N.

D. Gultekin, M. Uysal, S. Aslan, M. Alaf, M.O. Guler, H. Akbulut, The effects of applied load on the coefficient of friction in Cu-MMC brake pad/Al-SiCp MMC brake disc system, Wear 270 (2010) 73–82.

9.6 Metals in railway brakes

Although in the last few years sintered MMC have been the most appealing materials for use in high-speed trains, metallic materials were already present, such as in brake blocks made of cast iron, for decades. The different braking conditions (low pressure) in comparison with other ground vehicles reveal new aspects of metals in friction materials. For example, the introduction of small amounts (between 0.4 and 2 wt.%) of Cu and Sn improve the wear performances of traditional gray cast iron brake shoes, favoring the increase of the pearlite eutectoid [10]. Fe–Cu–Cr–graphite sintered materials exhibited less sensitivity to speed than gray cast iron, also in pin-on-disk studies

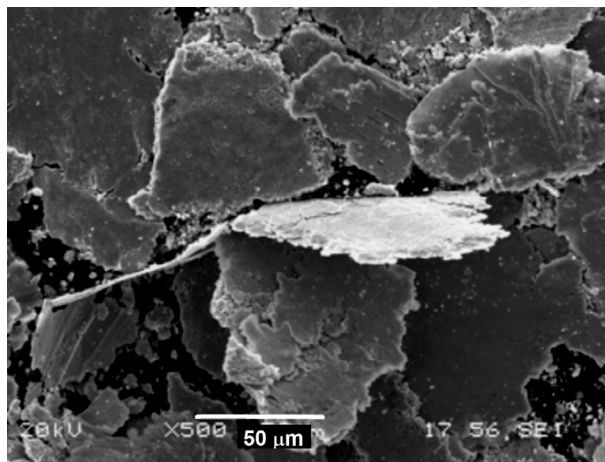


Figure 9.7 Wear debris morphology of pad composites that contained 2.0 wt.% of graphite at 20 N load and 0.5 m s^{-1} sliding velocity [8].

carried out by Ferrer et al. [11], together with a smoother rotor surface, probably delivering less noisy brakes and more suitability for high-speed trains. The problem of nanoparticle release in air should also not be underestimated, especially for metallic shoes or pads, since it seems to be very huge in comparison with composite materials, as reported by Olofsson for cast iron materials [12], as previously mentioned.

It should not be forgotten that railway disks are made of metal, for instance steel, and their wear is affected by the metallic elements of the alloy. One of the most worrying problems is that of crack damage, which concerns both safety and lifetime of the brake parts. For instance, cracks in rail steel wheels are connected with both thermal expansion compressive stress (due to brake blocks) and rolling compressive stress [13]. Ni–Mo–Cr steel with high martensite hardenability, such as A4340 rotors, is currently used for high-speed trains, overcoming 300 km h^{-1} . The risk of heat cracks is increased and consequently influences the ongoing search for reliable alloys and materials. For example, the addition of 0.1% of V to a Ni–Mo–Cr steel improves heat shock resistance, toughness and hardness. Cracks due to heat are considerably decreased in specific dynotests [14]. However, wear resistance is reduced, indicating that this search is not ended and will continue until a material is found with adequate hardness of the friction surface conjugated to low hardenability.

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10.1 Introduction

The history of phenol formaldehydes (PFs) is very long. Their compelling commercial entry was mainly due to Leo Baekeland who, while engaged in the search for synthetic resins, synthesized a polymeric plastic based on PF in 1907, called bakelite. It had many applications, for example as an electrical insulator and in other electrical components and products such as telephones. Baekeland investigated the reactions of phenol and formaldehyde, first producing a soluble phenol–formaldehyde to substitute for shellac, called Novolac, which never became a market success. Afterwards, he turned to developing a phenol–formaldehyde binder for asbestos, which at that time was molded with hard natural rubber. Since the first friction materials for combustion engine vehicles were basically made of large amounts of asbestos, this explains why PF resin began to be used as a binder in this field. In fact, the most established binders for friction materials belong to the PF family, which is characterized by high mechanical properties, thermal stability up to 350–450 °C, and enough toughness to resist friction thermo-mechanical stresses. Currently, the most used PFs in the friction field are novolacs, as the more unstable resols are less common. Note that it is not the purpose of this chapter to deal with the detailed reaction conditions and production processes of PFs, which have already been deeply and widely described and presented by Gardziella et al. [1], nor the standards used to control the effectiveness and quality of PFs.

However, specific and accurate information on both synthesis and products is provided, because such information can help materials engineers to discuss with PF technicians and promoters both performance and quality objectives in relation to friction materials. Other typical organic components of friction materials are rubber, such as nitrile-butadiene rubber (NBR), styrene butadiene rubber (SBR), and fibers such as polyacrylonitrile (PAN) fibers, aramid fibers, cellulose fibers, and the so-called friction dust. Small amounts of plasticizer are also used. The utilization of silanes and polysiloxanes is starting but is limited by costs. Also polyethylene (PE) and polyethylene terephthalate are used in small amounts, less than 2 wt.%. It is possible that new inorganic or hybrid binders will be created to reduce or even completely remove the use of formaldehyde. Some use of melamine formaldehyde resins is common among clutch manufacturers and mixing melamine and phenolic resins in certain cases offers some advantages in brake pads. Benzoxazine-modified resins and high ortho-phenolic resins are also available, as well as fast-curing resins to satisfy high-rate production needs and special performances. It is also possible to use other aldehydes, such as furfural, etc., as cross-linking agents.

Each organic component has a function: structural in the case of resins and fibers, both structural and noise damper for rubbers. Organic components are subject to a different type of wear, which is an oxidative wear in which most material removal is due to the gas CO₂. Previous to this phase there is decomposition in which a carbonaceous

amorphous phase is usually formed. The external layer of worn friction material surfaces, which has a variable thickness of several micrometers, is made of a composite containing decomposed organics; the wear resistance may also depend on the continuity between the decomposed organic matrix and the bulk matrix. The failure or lack of a gradual change between the carbonized and the bulk organic binder may cause severe wear. Several factors may contribute to this situation, but the main ones are two: the chemical nature of the organic matrix (binder), and heat dissipation. Heat dissipation was discussed in the previous two chapters. In this chapter, the relationship among chemical bonds, structure of the organic materials and the final properties of friction materials will be discussed.

10.2 PF resins

The reagents used to obtain PF resins are phenol and formaldehyde. The reaction can be promoted by either base or acid catalysts. Phenol is characterized by having essentially three reactive sites: two *ortho* positions and one *para* position. Novolacs are obtained with a formaldehyde to phenol molar ratio less than 1 and are catalyzed by either organic or inorganic acids such as oxalic acid, sulfuric acid, phosphoric acid, etc. On the other hand, resols are obtained with a formaldehyde to phenol molar ratio greater than 1, usually 1.5, in a reaction catalyzed by bases at temperatures between 40 and 120°C. The type of final resin depends to a large extent on the molar ratio of formaldehyde to phenol as well as the type of catalyst, e.g., acidic or basic. Indeed, the catalyst type influences the rate of reaction of phenol and formaldehyde and the final properties of the resins. The reaction consists of two steps: the first is the electrophilic attack of formaldehyde to form hydroxymethyl groups, and the second is the attack of hydroxymethyl to an available either *para* or *ortho* position of another phenol to form water, as shown in Figure 10.1.

Resols are produced at temperatures between 40 and 120°C using an alkali catalyst, either an inorganic catalyst such as NaOH or $Mg(OH)_2$ or an organic one such as tertiary amino alcohols [2]. The reaction is controlled by the type and quantity of catalyst and the temperature. High alkali concentrations (up to the molarity of the hydroxyl phenolic group) in combination with low temperatures promote and stabilize hydroxymethyl groups (resols), while low catalyst concentrations and high temperatures promote the condensation reaction leading to a thermoplastic resin (novolac).

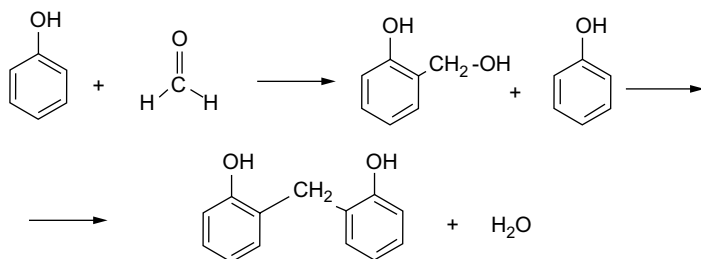


Figure 10.1 The two steps of the synthesis of PFs.

These are used less and less because they are very reactive, which causes storage, transport, and handling problems. Moreover, in resols there are unreacted hydroxymethyl groups (for example, during curing), which can further react with the hydroxymethyl groups of other phenol polymers to form methylene bridges, producing water and formaldehyde, or they can form ether bridges producing water, according to the simple examples of Figure 10.2, which involve two resol dimers. However, the formation of ether bridges is faster than that of methylene bridges.

The methylene bridges in resols are favored by cross-linking (curing) above 150 °C, and a study executed by Lenghaus et al. [3] showed that an *ortho* quinone methide is formed by dehydration (see Figure 10.3). The latter only attacks the *ortho* position of another phenol contributing to a higher ratio of *ortho* to *para* cross-linking positions.

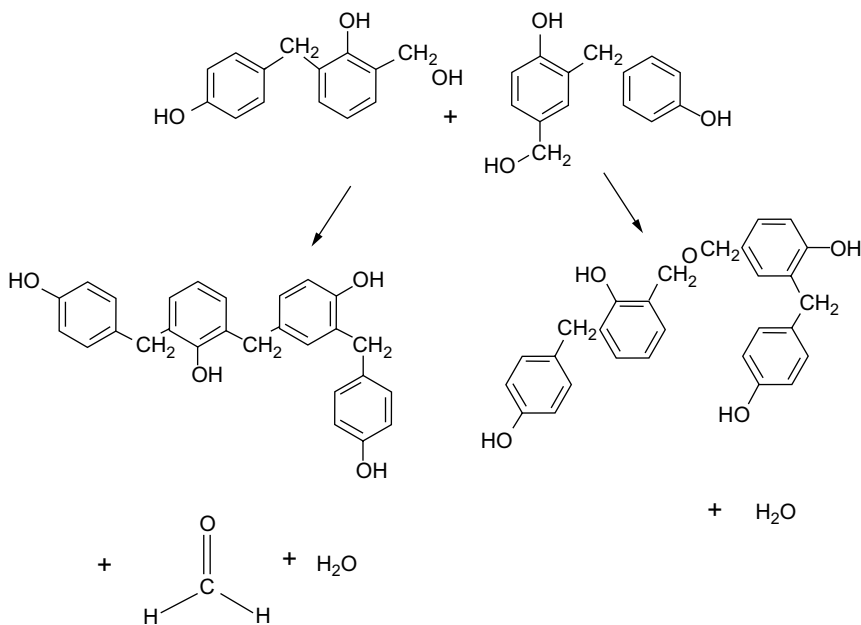


Figure 10.2 Condensation reaction of two resol dimers forming either methylene or ether bridges.

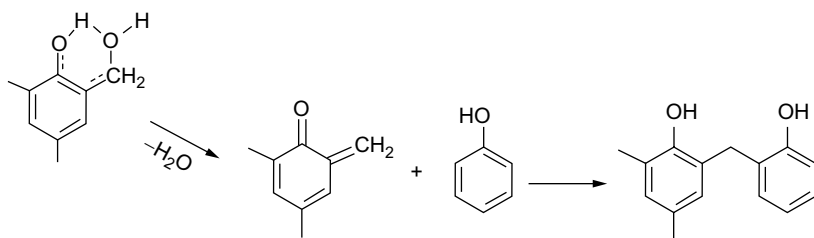


Figure 10.3 *Ortho* quinone methide pathway toward methylene bridges in resols.

The polymers obtained during novolac synthesis can contain several phenol units with a variable combination of *o-p*, *p-p*, and *o-o* methylene linkages, such as the dimer bisphenol F, shown in Figure 10.1. All the types of linkages can be present in the same polymer chain, giving origin to a great variety of polymer types more or less linear. However, although the usual distribution of the types of linkages, as stated, is more or less random (reminding one that the *para* position is more reactive), it is possible to favor a combination *o-o* to obtain a high *ortho* resin. The substitution of phenol with formaldehyde in the *ortho* position versus *para* position increases in the following sequence of hydroxide catalyst metals: $K < Na < Li < Ba < Sr < Ca < Mg$. Typical distributions of linkages are reported in Table 10.1 for some types of novolacs [4].

In novolacs there are no free hydroxymethyl groups, due to the deficiency of formaldehyde during synthesis, which was all involved in forming methylene bridges in the polymer. Novolac cross-linking can be carried out only by adding a cross-linking agent able to decompose by thermal treatment and attack the phenolic aryl ring, such as hexamethylenetetramine (HEXA).

Figure 10.4a and b shows fragments of cross-linked resol and novolac.

The molecular weight distribution of the PF polymers that will cross-link during the curing phase determines and defines the final product characteristics as well as the degree of polymerization, as any prevalence of the type of linkages between phenols and the amount of HEXA. For example, the greater availability of the *para* position in high *ortho* PFs, which is more reactive than the *ortho* position, can provide *very fast-curing* resins. Another important aspect is the type of modification, meaning the possible groups or chains linked to the aryl ring of phenols, which confer special properties of the cured resin.

Table 10.1 Distribution of linkages in novolacs [2]

Novolac type	Ratio <i>ortho</i> to <i>para</i>
High <i>ortho</i>	75:25
Normal	45:55
High <i>para</i>	38:62

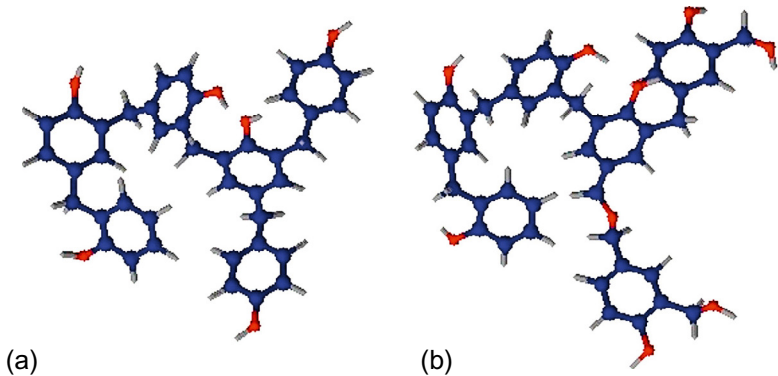


Figure 10.4 (a) Fragment of cross-linked novolac; (b) fragment of cross-linked resol.

10.3 Cross-linking agents

Cross-linking agents are added to novolacs to create bridges among the novolac polymers, i.e., the process of curing. Among them, the most common is hexamethylenetetramine (in short known as HEXA), which decomposes and reacts with a considerable rate from 150 °C and formally provides six methylenes per molecule. The cross-linking reaction usually passes through several stages to form methylene bridges. However, a certain amount of nitrogen is retained in the structure depending on the initial HEXA content. Resols can act as cross-linking agents for novolacs but are poorly utilized for the previously mentioned reasons. Triazines formaldehyde polymers can be also used as curing agents to form a copolymer with novolacs. These copolymers can have interesting properties, with reduced wear, and are especially used in clutches. The most common triazine curing agents are based on melamine formaldehyde resin or benzoguanamine. The reaction is similar to that of resols but needs temperatures usually between 150 and 200 °C to be carried out quickly, and the reaction is favored by acid catalysts. This kind of cross-linking is very sensitive to the applied pressure and content of melamine formaldehyde. An investigation carried out by Dante et al. [5,6] showed that a high weight ratio of melamine to novolac such as that of 1:1 provides a better thermal stability with an applied pressure of 150 MPa at 200 °C. However, lower ratios of 1:5.7 of melamine to novolac provide better results with the lower applied pressure (20 MPa) and high temperature (200 °C). The differential scanning calorimetry (DSC) shows that the cross-linking occurs at a highest rate around 200 °C, and it is characterized by a broad exothermic band which possibly is due to a direct cross-linking between phenol and melamine polymers. The DSC curves of the samples B and D of Figure 10.5 belong to samples treated at 150 and 200 °C with pressure at 20 MPa, while C was treated at 200 °C and 140 MPa. The reactions of samples treated at 200 °C are accelerated. The broadness (interval between 160 and 225 °C) is probably due to the great variety of linkages formed between triazine units and phenols, for instance including ether bridges $-\text{CH}_2-\text{O}-\text{CH}_2-$, $-\text{NH}-\text{CH}_2-\text{NH}-$, and $=\text{N}-\text{CH}_2-\text{N}=-$.

Benzoxazines, which are intermediates of the reaction with HEXA, can be curing agents too. They react with PF polymers to form a final cross-linked resin. The benzoxazines that may be used in combination with PF are usually based on bisphenols A and F (see Figure 10.6) and phenolphthalein. Curing occurs much quicker above 200 °C.

The thermosetting resin so obtained may exhibit a better wear of both brake pad and rotor.

10.4 Cross-linking kinetics

Resols have a variable activation energy that varies with the reaction advancement, as evidence that the mechanism of reaction varies with advancement. Indeed, the activation energy E_a can vary between 60 and 120 kJ mol⁻¹ as found by thermal-kinetics studies [7]. This indicates that the cross-linking reaction passes through several stages. The average molecular weight is also affecting the rate of cross-linking; higher molecular weight resols can reach their highest rates at lower temperature at a low degree

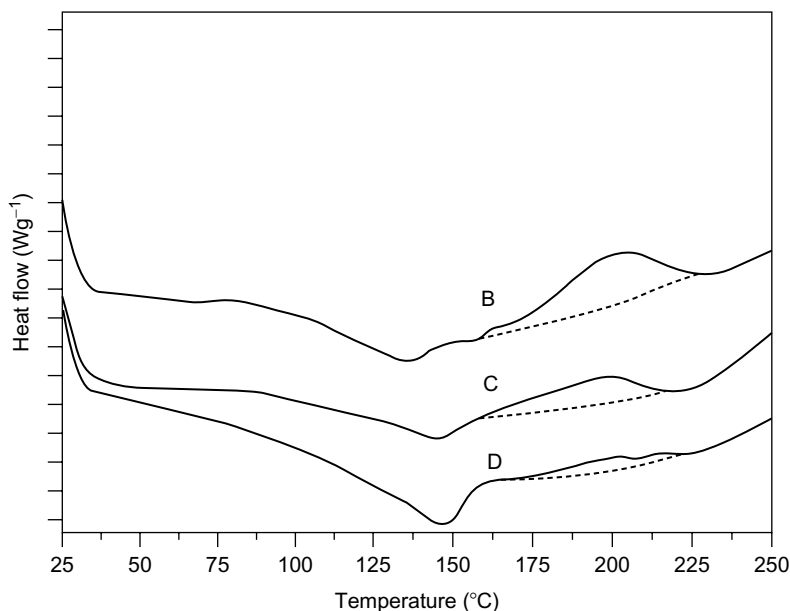


Figure 10.5 DSC curves of samples B (150 °C, 42 min, 20 MPa), C (200 °C, 45 min, 140 MPa), D (200 °C, 45 min, 20 MPa) [5].

R.C. Dante, D.A. Santamaria, J. Martín Gil, *Crosslinking and thermal stability of thermosets based on novolac and melamine*, *J. Appl. Polym. Sci.* 114 (2009) 4059–4065.

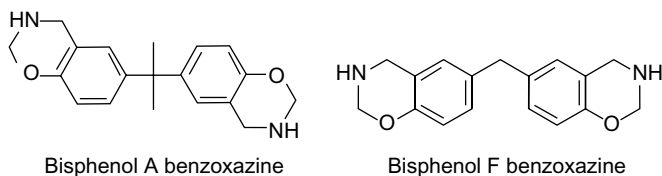


Figure 10.6 Benzoxazines based on bisphenols A and F, respectively.

of cross-linking advancement. These characteristics are especially important for resol adhesives. The cross-linking rate can be incremented using alkaline compounds such as sodium carbonates or magnesium oxide.

The initial cure of novolacs is a homogeneous acid-catalyzed reaction involving traces of water to hydrolyze HEXA into α -amino alcohols. The acidic phenolic units generate carbonium ions from these α -amino alcohols, which then react with phenolic units to form benzylamines. This fact is evidenced by the increase in the reaction rate with decreasing pH for both the novolac resins and model systems and increasing phenol or water content. Excess water could decrease the reaction rate. Although higher amounts of HEXA lead to shorter gelation times, the activation energies E_a , obtained from rheokinetics data [8], were 57.1, 68.8, and 87.3 kJ mol⁻¹ for novolac to HEXA weight ratios of 93:7, 91:9, 89:11, respectively. This is probably due to the fact that

novolacs with high content of HEXA with a growing network behave more as a solid with a reduced mobility that increases the final E_a .

10.4.1 Fast-curing resins

The cross-linking reaction of novolacs with HEXA is exothermic and becomes rapid in the interval of 140 and 160 °C. Most research in friction material processes was focused on decreasing the molding and curing process, and for this purpose fast-curing resin were developed. Every methylene in HEXA can attach to reactive sites giving origin to intermediates that need other available reactive sites. In fact, different ratios of reactive sites in novolac polymers to HEXA methylenes have different rate behaviors. Benzylamine and benzoxazine (shown in Figure 10.7a and b) are some of the common intermediates of the reaction of novolac polymers with HEXA, which can further react with free active sites, i.e., either *ortho* or *para* free positions.

In the case of higher ratios of HEXA methylenes (remember that each HEXA has six methylenes), there are not enough free sites available for intermediates to cross-link, causing a situation of high density of cross-linking. Thus cross-linking is very slow for the few free sites available. The reaction of cross-linking can be divided into two stages as follows:



The rate of the second stage (Equation 10.2) can be increased by a high ratio of free sites to intermediates; otherwise, intermediates will not find available sites to cross-link. Thus, fast-curing novolacs are characterized by a low ratio of input HEXA (around 4 wt.%) to produce a low content of intermediates. The low content of HEXA also favors a lower pH, considering that novolacs are slightly acidic while HEXA is basic, which in turn favors the formation of the intermediates and their decomposition to the final products. This leads to a fast reaction rate but a low cross-linking density. A high *ortho* novolac might have an even higher rate considering that *para* available sites are more reactive. This, combined with higher content of HEXA, might lead to a fast curing with a high cross-linking density.

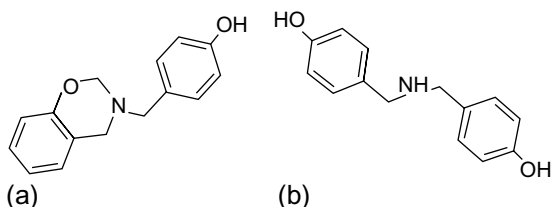


Figure 10.7 Steric representation of two simple intermediates of the reaction between novolac polymers and HEXA: (a) benzoxazine, (b) benzylamine.

10.5 Thermal decomposition of PF

PFs decompose thermally producing several volatile by-products as well as carbonizing glassy carbon. The failure of the binder is essentially due to the pyrolysis process. From thermogravimetric analysis three stages can be distinguished with different activation energies, the lowest around 200 kJ mol^{-1} and the highest around 300 kJ mol^{-1} [9].

In the first stage, around 300°C there is a further cross-linking involving the hydroxyl group to form water; the second stage around 500°C is due to the instability of the methylene bridges. In this stage phenol, *o*, *p*-cresol and *o*, *p*-xylene are the main volatile by-products; in the third stage around 650°C , benzene, toluene, xylene and huge amounts of CO and CO_2 as well as H_2 are released, while an amorphous carbon phase is formed. In this last phase the hydroxyl radicals provide an oxidative atmosphere for methylene. However, oxidation is not responsible for the decomposition of the resin [10].

10.6 Boron and phosphorus modified PF resins

The decomposition of PF resins and in air their oxidative loss can be reduced and retarded by modifying the resin with boron. This modification confers a higher thermal stability, flame retardancy, and heat resistance properties. The boron modification is obtained by introducing boric acid during the synthesis of the polymers; almost all the boron is finally linked to methylene through an oxygen bridge such as in Figure 10.8. Moreover, boron-modified resins can be synthesized from triphenyl borate [11].

Studies conducted with bisphenol A to form a boron-modified PF showed that the conversion rate of the reaction of benzyl alcohol with boric acid was over 50% in 50 min at 120°C , while it was only 4% in 150 min in the reaction of phenol with boric acid. During the curing process the hydroxyl group also can react with boron.

In general, boron bonded to the phenoxy group can also be found, as shown in Figure 10.9 where a boron atom is linked to three phenoxy groups [12]. However, intermediate cases are possible with methylene linkages. This structure may be formed during curing or thermal treatments, like those which friction materials undergo. To a certain extent, however cross-linking increases, it can be considered the first stage of decomposition of this type of resin.

An alternative structure was proposed by Gao et al. [13] based on a study of a bisphenol F boron-modified resin, which is a hybrid situation between the cases of Figures 10.8 and 10.9. In Figure 10.10 this situation is illustrated, where B forms a coordination bond with the oxygen atom of the phenol hydroxyl. In this case two

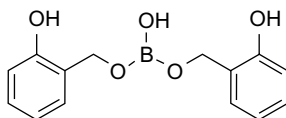


Figure 10.8 Boron atom linked to two methylene ether bridges. A borate bond B–O is still present.

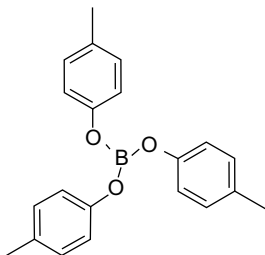


Figure 10.9 Boron atom linked to three phenoxy groups.

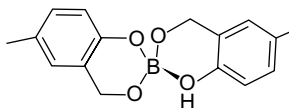


Figure 10.10 Coordination bond of oxygen with boron.

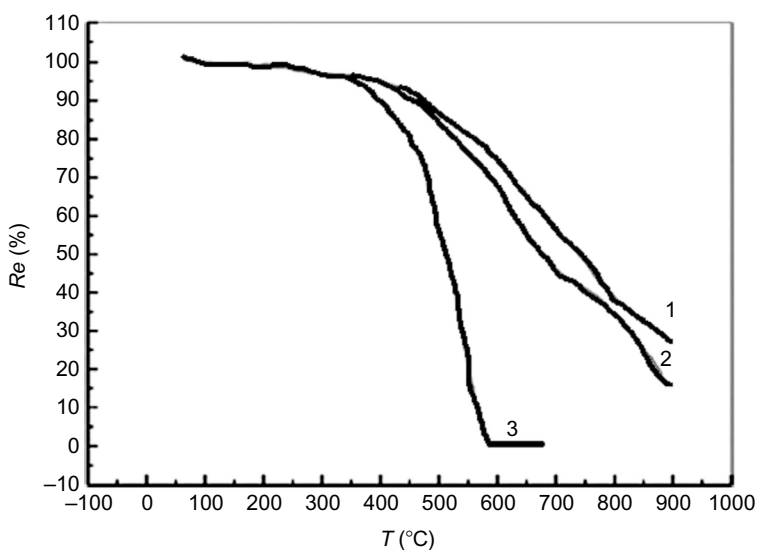


Figure 10.11 Thermogravimetric analysis of boron-modified resin: (1) 1.6B, (2) 1.0B, (3) 0.0B at heating rate of $10^{\circ}\text{C min}^{-1}$ in air.

J. Gao, L. Xia, Y. Liu, Structure of a boron-containing bisphenol-F formaldehyde resin and kinetics of its thermal degradation, Polym. Degrad. Stabil. 83 (2004) 71–77.

six-membered rings, including the B atom, are formed, and the borate bond B–OH is disappeared at curing temperatures above 140°C .

The benefit of the boron modification is the increased thermal stability of the resin that makes it especially suitable for heavy-duty brake applications, which undergo considerable thermo-mechanical stresses and must dispose of a huge amount of heat. In [Figure 10.11](#) three thermal gravimetric curves of boron-modified PFs are shown

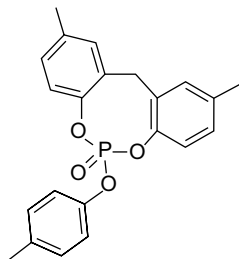


Figure 10.12 Phosphate linked to phenoxy groups.

with different values of borate number, which is the ratio of the IR absorption of the B–O bond at 1350 cm^{-1} to that of aryl ring absorption at 1600 cm^{-1} , taken as reference. The borate number in uncured resins was used to estimate the boron content.

It is possible to modify PF resins with phosphorus using phosphoric acid. In this case, phosphate will be linked to phenoxy groups in a similar manner as boron [14], as shown in Figure 10.12. Moreover, these resins exhibit a high thermal stability similar to the boron-modified PF resins, and are a feasible alternative for heavy-duty applications.

10.7 Molecular weight

As can be understood, many of the binder properties, such as thermal stability, stiffness, toughness, and viscoelasticity are affected by the molecular weight of the polymers. Many properties such as tensile strength are eventually saturated due to large molecular weights, asymptotically approaching the limit case of an infinite polymer, as expressed in the following equation:

$$P = P_{\infty} - \frac{C}{M} \quad (10.3)$$

where P is the value of the considered property, P_{∞} is the value at infinite molecular weight M , while C is a constant.

Cross-linking, whether considered as a second phase of polymer growth, only partially compensates for a low average molecular weight. In fact, this is a determining parameter to be taken into account by materials engineers. However, polymer length varies depending on the reaction conditions, and consequently the distribution of molecular weights of the polymers varies, and this phenomenon causes so-called polydispersion. For this reason, there are different ways to express an average molecular weight and calculate polydispersion. These parameters are currently underestimated by friction materials engineers; nevertheless they are implicated in many of the incomprehensible performance variations of homologated friction materials.

The number average molecular weight $\bar{M}_N$ is expressed in the following way:

$$\bar{M}_N = \frac{\sum_i N_i M_i}{\sum_i N_i} \quad (10.4)$$

where M_i and N_i are the molecular weight and the number of molecules with length i (number of repeated basic units of monomer), respectively.

As implied by Equation (10.4), $\bar{M}_N$ can also be expressed in term of the molar (number) fraction of the i th polymers:

$$\bar{M}_N = \sum_i X_i M_i \quad (10.5)$$

In most cases, weight is more easily measured than moles. If we consider the weight fraction instead of the molar fraction, we obtain another molecular weight, called *weight average molecular weight* $\bar{M}_w$, in which the polymers with the highest weight fractions “weigh” more.

$$\bar{M}_w = \sum_i w_i M_i \quad (10.6)$$

where w_i is found by:

$$w_i = \frac{M_i N_i}{\sum_i M_i N_i}$$

Moreover, $\bar{M}_w$ can be rewritten in terms of the molar fraction and we obtain the following equation:

$$\bar{M}_w = \sum_i \frac{N_i M_i}{\sum_i N_i M_i} M_i \quad (10.7)$$

Observing the forms of Equations (10.5) and (10.7), it is possible to generalize the average molecular weight in this way, considering powers of M_i :

$$\bar{M}_k = \sum_i \frac{N_i}{\sum_i N_i M_i^k} M_i^{1+k} \quad (10.8)$$

where with $k=0$ and $k=1$ we have $\bar{M}_N$ and $\bar{M}_w$, respectively. With $k=2$ and $k=3$, the so-called $\bar{M}_z$ and $\bar{M}_{z+1}$ are obtained. Each of these molecular weight expressions can have some usefulness depending on the studied property; in addition, they provide information on the real distribution of molecular weights.

All these molecular weight values are usually different, and the magnitude order is the following:

$$\bar{M}_N \leq \bar{M}_w \leq \bar{M}_z \leq \bar{M}_{z+1} \leq \bar{M}_4 \quad (10.9)$$

The equality case in Equation (10.9) can be reached only for a monodispersed polymer. The proper definition of a coefficient of polydispersion can be found by analyzing the statistics concerning polymer distributions. However, monodispersion corresponds to polymers all of the same length; a situation that never occurs in synthetic products. A possible molecular weight distribution corresponding to a chromatogram by gel permeation (GPC) is shown in Figure 10.13, indicating the position of the molecular weight exposed in Equation (10.9).

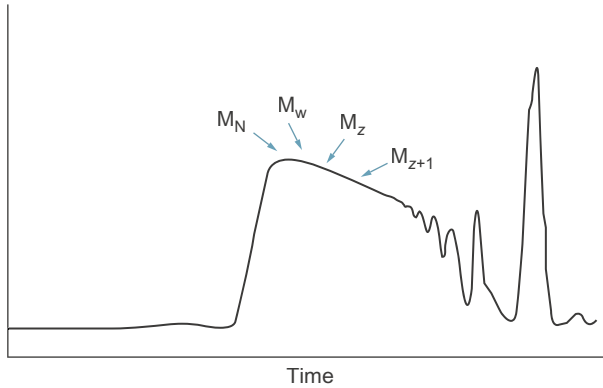


Figure 10.13 GPC chromatogram of a PF resins with molecular weights positions.

10.7.1 Statistics of molecular polymer weights

The standard deviation of molecular weights is defined in the following way:

$$\sigma^2 = \bar{M}^2 - \bar{M}^2 \quad (10.10)$$

With some mathematical manipulation, it is possible to arrive at the following expression:

$$\sigma^2 = \frac{(\sum_i N_i M_i) \sum_i N_i M_i^2}{(\sum_i N_i M_i) \sum_i N_i} - \left(\frac{\sum_i N_i M_i}{\sum_i N_i} \right)^2 \quad (10.11)$$

It is possible to recognize that by dividing and multiplying the first term of Equation (10.10) by the same factor $\left(\frac{\sum_i N_i M_i}{\sum_i N_i} \right)$, the standard deviation can be expressed as composed of M_N and M_w :

$$\sigma^2 = \bar{M}_N \bar{M}_w - \bar{M}_N^2 = \bar{M}_N^2 \left(\frac{\bar{M}_w}{\bar{M}_N} - 1 \right) \quad (10.12)$$

It is noteworthy to mention that the standard deviation is null only when $M_w = M_N$, i.e., we have a monodisperse polymer. Therefore, the polydispersity index is expressed as the ratio M_w/M_N .

This index for real synthetic polymers is always greater than 1:

$$\frac{\bar{M}_w}{\bar{M}_N} \geq 1 \quad (10.13)$$

Moreover, the coefficient of variation (CV) exclusively depends on the polydispersity index:

$$CV = \frac{\sigma}{M_N} = \sqrt{\frac{\bar{M}_w}{\bar{M}_N} - 1} \quad (10.14)$$

which may be real exclusively, satisfying Equation (10.13).

10.7.2 The Flory distribution

For a given extent of reaction and a given monomer composition, it is possible to determine the probability of the polymer distribution, i.e., to find the most probable distribution of polymers. This distribution is named the Flory, or sometimes Flory–Schulz, distribution, from the pioneers in the study of polymer chemistry [15]. It is possible to summarize the basic theory in the following way: if A and B are two functional groups, such as the *ortho* or *para* positions of phenol and formaldehyde, reacting by condensation, considering A–B as the monomer, and p is the fraction of reacted A sites (always $p \leq 1$, while the unreacted fractions of A and B are simply $1 - p$). For a polymer with ending group A, the probability that the adjacent B is unreacted is simply $1 - p$, which thus corresponds to the fraction of the monomer A–B:

$$p(i = 1) = 1 - p \quad (10.15)$$

For the dimer (A–B)₂ the probability is given by the product between the probability that the first group –A (named A₂ in Equation 10.16) is reacted by that of the second group –B (named B₂ in Equation 10.16) is unreacted:

$$A_1 - B_1 - A_2 - B_2 \equiv (A - B)_2 \quad (10.16)$$

$$p(i = 2) = p(1 - p) \quad (10.17)$$

based on this sequence the probability that the polymer has a degree of polymerization i (polymer length) is:

$$p(i) = p^{i-1}(1 - p) \quad (10.18)$$

As can be inferred, the monomer always has the highest probability (fraction) to be found.

If there are N molecules in the reaction environment, the molecules with length i are given by:

$$N_i = Np^{i-1}(1 - p) \quad (10.19)$$

N is related to the initial total number N_0 , and is given by $N = N_0(1 - p)$, thus the most probable Flory distribution becomes:

$$N_i = N_0p^{i-1}(1 - p)^2 \quad (10.20)$$

which is approximately followed by all condensation polymers such as PF resins.

The weight fraction of the polymer i can be expressed as the function:

$$w_i = \frac{iM_0N_i}{M_0N_0} = ip^{i-1}(1 - p)^2 \quad (10.21)$$

where M_0 is the repeating unit molecular weight in the polymer. As the reaction extent p increases to the end of the reaction, the distribution broadens and the higher

polymers weigh more in the distribution. In this case, it is possible to accurately calculate the number average molecular weight $\bar{M}_N$:

$$\begin{aligned}\bar{M}_N &= \frac{\sum_{i=1}^{\infty} i M_0 N_i}{\sum_{i=1}^{\infty} N_i} = \frac{M_0 N_0 (1-p)^2 \sum_{i=1}^{\infty} i p^{i-1}}{N_0 (1-p) \sum_{i=1}^{\infty} p^{i-1} (1-p)} \\ &= \frac{M_0 (1-p) \sum_{i=1}^{\infty} i p^{i-1}}{\sum_{i=1}^{\infty} P(i)} = M_0 (1-p) \sum_{i=1}^{\infty} i p^{i-1}\end{aligned}\quad (10.22)$$

Equation (10.22) was obtained by combining Equations (10.21), (10.20), and (10.18). The evaluation of the sum requires the use of some artifice:

$$\sum_{i=1}^{\infty} i p^{i-1} = \frac{d}{dp} \sum_{i=1}^{\infty} p^i = \frac{d}{dp} \left(\frac{p}{1-p} \right) = \frac{1}{(1-p)^2} \quad (10.23)$$

Thus $\bar{M}_N$ becomes:

$$\bar{M}_N = \frac{M_0}{1-p} \quad (10.24)$$

With an analogous reasoning we can determine $\bar{M}_w$, and obtain:

$$\bar{M}_w = M_0 \left(\frac{1+p}{1-p} \right) \quad (10.25)$$

Therefore, the polydispersity index turns out to be:

$$\frac{\bar{M}_w}{\bar{M}_N} = 1 + p \quad (10.26)$$

As the degree of polymerization (extent of reaction) p approaches 1, the polydispersity index approaches 2—that is, a CV of 100%! Moreover, both $\bar{M}_N$ and $\bar{M}_w$ approach infinity, thus indicating the formation of a single long polymer chain.

A way to keep the molecular weight under control is to control the ratio of the two monomers. The molar ratio of N_A to N_B , now with A–A and B–B being the two monomers (instead of A–B), is named r :

$$r = \frac{N_A}{N_B} \quad (10.27)$$

In this case, we have a limiting reagent that will stop the reaction at a desired average molecular weight. This method requires an elevated control upon r to avoid molecular weights either too low or too high. The probability that an A group has reacted is given by:

$$p = \frac{N_A - N'_A}{N_A} \quad (10.28)$$

The probability q that a B group has reacted is related to the probability that an A group (see Flory's paper [16]) has reacted and is given by:

$$q = rp \quad (10.29)$$

M_N will take the following form as a function of r and p :

$$M_N = M_0 (1 + r) / (1 + r - 2rp) \quad (10.30)$$

This equation reduces to Equation (10.24) when $r=1$, reminding us that in Equation (10.30) the molecular weight M_0 is half of M_0 , i.e., the half of the repeating unit. For $r=0.95$ and at completed reaction $p=1$ the molecular weight calculated by Equation (10.30) is $M=39M_0$.

In the case of PF resins, a similar method is used to have either novolacs or resols. High molecular weight can be achieved with careful control of r .

10.8 Phosphorus acid phase separation

It is possible to obtain a narrow distribution of molecular weight using a method known as phosphorus acid phase separation (PAPS) developed by the Asahi research team [17–19], reaching a polydispersity index below 2 and close to 1 for low molecular weights, in comparison with values that are usually above 2 when obtained by using the conventional methods with oxalic acid. In this method 25 mass parts of phosphoric acid are used for 100 mass parts of phenol. This is a method in which two separate phases are formed. One phase is rich in phenol while the other aqueous phase contains phosphoric acid and formaldehyde. This is a way to keep and control the values r and p (described in the previous section) close to a desired value in the reaction interface during the total reaction, thus favoring the formation of the dimer, for example [20], or reducing the polydispersity index, and consequently the CV of the molecular weight distribution. A high ratio of P:F (between 0.8 and 0.9) will involve a phase transfer of the dimer to the organic phenol phase thus leading to high molecular weight novolacs with a polydispersity index between 1.5 and 2, which may have an application in the friction industry with a very low content of free phenol. The thermal stability of the PAPS resins is higher than that of conventional resins and this will be a benefit in friction materials, considering the strong demand for low wear friction materials since thermal (oxidative) wear will be dramatically decreased.

10.9 Friction powder

Another organic material which, from the chemical point of view, can be considered a fully cross-linked PF resin is the so-called “friction powder,” which derives from cardanol oil, extracted from the cashew nut shell and in fact also named cashew nut shell liquid (CNSL). This is a phenol with an alkylic side chain of 15 carbon atoms with some unsaturations, between 1 and 3, in the meta position (see Figure 10.14), which allow polymerization through the side chain. The powder obtained by polymerization of cardanol with formaldehyde leads to a brownish solid material used as low

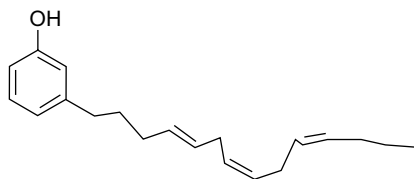


Figure 10.14 Cardanol (CNSL) molecule view showing the flexibility of the alkylic chain.

density filler with a certain ability to stabilize the coefficient of friction, lubricating, and decreasing noise. Cardanol is a compound completely compatible with PF resins, so there are many CNSL modified resins. The long alkylic chain provides more flexibility to the resin structure as well as better damping characteristics.

10.10 Rubbers and elastomers in friction materials

Rubbers of different types are used in friction materials to improve noise and vibration damping, as well as to favor adhesion as in the case of silicon-modified rubbers. Also PE is sometimes used for its ability to form films. Nitrile rubbers are very common in current formulations, both in the standard and cross-linked versions. Acrylonitrile butadiene rubbers (NBR) are obtained from propenenitrile and butadiene monomers such as 1,3-butadiene and 1,2-butadiene. The nitrile content (CN) in the butadiene groups is referred to as the ACN; the lower the ACN content, the lower the glass transition. There are also HNBR (a fully saturated version of NBR, where H stays for hydrogen) and XBR with carboxyl groups on the double bonds of butadiene, which can form bridges alternative to the classical sulfur ones. These carboxylic groups are present in 10% of sites or less. The bridges will be ionic bridges with Zn^{2+} linked to two carboxylic groups.

As stated, the ACN content is very important and determines the glass transition temperature as well as other properties; with 18% of ACN the T_g is around -40°C , while with 48% it is close to 0°C .

It should be noted that on the friction surface NBR will be not present during use because it dramatically decomposes above 350°C [21], which is a usual surface temperature.

SBRs and ethylene propylene diene monomer (EPDM), which is a terpolymer (i.e., obtained from three different types of monomers), are much less common due to their lower thermal stability. The diene of EPDM can vary, the most common one being 1,4-hexadiene. Much less frequently used are silicone rubbers since they exhibit poor wear resistance. Neoprene rubbers (also identified as CR), i.e., formed by polymerization of the monomer 2-chloro-1,3-butadiene, were more commonly used when rubber was introduced with solvents such as trichloroethylene. Currently most rubbers are introduced and used in powder form in friction material blends in order to avoid toxic and dangerous solvents. Fluoroelastomers encounter some use because they improve temperature resistance but prices limit them to a lean content in formulas. The chain repeating units of some of the polymers mentioned are shown in Figure 10.15. The most usual cross-linking agent is sulfur; however, the utilization of cross-linked rubbers is increasing because it allows to avoid to use sulfur, a component to be mixed in a so low amount to be ineffective.

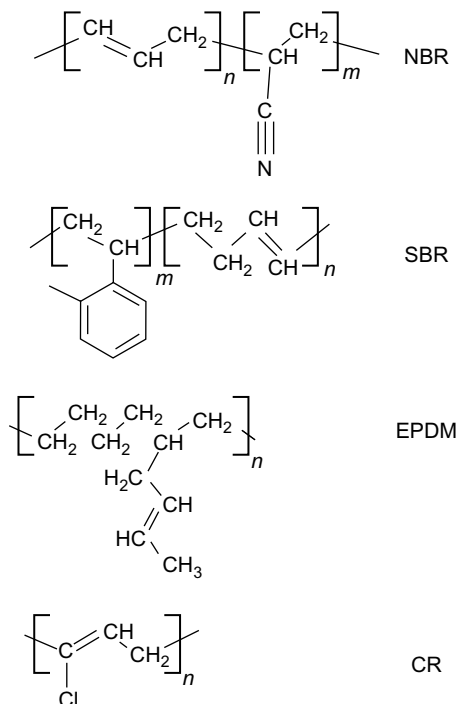


Figure 10.15 Types of rubbers: acrylonitrile butadiene (NBR), styrene butadiene (SBR), ethylene propylene diene monomer (EPDM) diene monomer: 1,4-hexadiene, neoprene (CR).

In the past, there was a tendency to prepare premixes with rubber to incorporate steel fibers in order to decrease their negative effect on noise. This practice will be abandoned due to the low content of steel fibers used in current materials.

10.11 Organic fibers

Aramid fibers and PAN fibers are both used in friction materials. They help in dry mixing in various ways: keeping components with different density together, in pre-forming, contributing to the mechanical strength, and increasing the wear resistance of the materials. PAN fibers are the precursors of carbon fibers obtained by pyrolysis. They are used in pulp and fibrillated forms to better mix and trap powder. Their content is usually around 2 wt.%. It is noteworthy to point out that the opening of fibers during mixing is a delicate task to be achieved with inorganic fillers.

The strength of aramid fibers is given by their structure, which includes strong interactions between adjacent polymer ribbons. These interactions provide a high thermal stability to this fiber, which made it the substitute candidate for asbestos. The name *aramid* stands for “aromatic polyamide” and its structure, which is a para-aramid, is shown in [Figure 10.16](#).

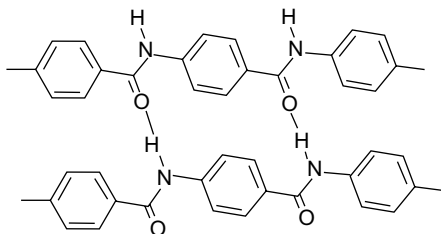


Figure 10.16 Interaction between adjacent ribbons of aramid fibers.

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