THERMAL CHARACTERISATION OF BRAKE PADS

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Abstract

The chemical-physical decomposition processes that occur in a brake pad heated to 1000°C have been studied. This temperature can be reached when a brake pad is applied. Thermogravimetry and differential thermal analysis were used in combination with evolved gas analysis, and image analysis using a scanning electron microscope.

A brake pad is essentially a mixture of iron, carbon and binder. Combined techniques have been used, because of chemical reaction overlap, to determine how and at what temperature the binder decomposes, the coal and graphite combust and the iron oxidises.

This work enables the development of brake pads that are stable at high temperature.

Keywords: brake pads, decomposition, oxidation, technical application of thermal analysis

Introduction

Recent years have witnessed a growth in industrial applications of thermal analysis and calorimetry. The present work is an example of the use of thermal analysis for an industrial purpose: the thermal characterisation of brake pads. The influence of the temperature on the wear and the friction of some brake pads has already been studied [1]. This present technical application is about the chemical-physical processes that occur when the temperature increases.

The new disc brake pads (Fig. 1, [2]) for automobiles and motorcycles consist typically of 10–20 different non-asbestos materials [3]. There is a series of different types of friction materials on the market, which can be classified into the following 3 categories: Semi Metallic (SM), Non Asbestos Organic (NAO), and Sinter Metal.

The sample analysed by thermal analysis belongs to the semi-metallic category [4]. It is mainly composed of a relatively large amount of iron powder and steel fibres, some graphite and coke, rubber, organic fibres, ceramic materials, abrasives, lubricant and filler. The mixture is bonded together by a thermosetting phenolic resin. Production of brake pads is typically performed in 4 steps: mixing of the ingredients, hot pressing of the powder onto the metal backplate, post-curing in a batch oven (temperature below 300°C), and finishing by painting, grinding and slotting.
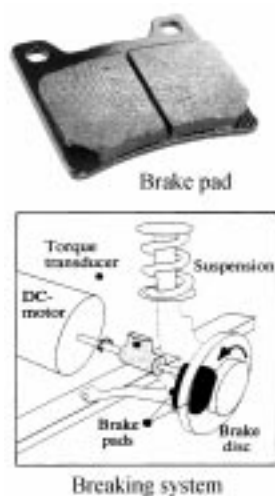
Fig. 1 Brake pad and braking system

When a brake pad is applied (Fig. 1), it rubs against the surface of a brake disc and leads to a diminution of the speed of the vehicle [4]. Activation of a brake system on a moving vehicle converts the kinetic energy of the vehicle into heat created by the friction force between the surface of the friction material and the brake disc or drum. During braking a temperature of +1000°C is occasionally observed on the friction material surface. Such high temperature implies a degradation of the material on the surface of the brake pad, with a gas evolution as a consequence. This gas evolution is experienced by the driver as a loss in braking action, which implies a risk of damage to the vehicle as well as to the driver.

Therefore, it is very important to obtain a new knowledge and understanding of the chemical-physical decomposition processes that occur when a friction material is exposed to severe thermal conditions. Differential thermal analysis (DTA), thermogravimetric analysis (TG), and evolved gas analysis (EGA) as well as optical analysis with a scanning electron microscope (SEM) have been used.

Experimental

Five different samples were analysed: the brake pad sample named X, and the 4 main raw materials composing this sample X, iron Fe, graphite G and coal C, and the binder system BS. To analyse the binder system a special sample named BS was prepared. Sample BS was based on sample X formulation, but all the raw materials, which were not a part of the binder system, were replaced with some quartz powder SiO_2. Therefore sample BS is only composed of binder and SiO_2. Apart from the crystallographic transformation of SiO_2, quartz-α to quartz-β at 573°C without mass change, the only reactions that will take place are due to the decomposition of the binder system. Sample BS was pressed and cured under the same conditions as X.

The equipment used for the DTA–TG is a Mettler nr.16 TA1. The evolved gas analysis has been made simultaneously using the mass spectrometer Stanton Redcroft STA 784. The method of analysis contained 3 steps. A first scan was made from room temperature to 1000°C at +2°C min^{-1}. The temperature was maintained at 1000°C for 1 h, and a final scan was made from 1000 to 25°C at –10°C min^{-1}. The samples were analysed in air with a flow of 87 ml min^{-1}.

To be in the best conditions for the analysis [5], all the samples were crushed to a maximum powder size of 125 μm. The same amount of powder was used for similar materials (coal and graphite were, for example, both tested with around 50 mg of powders). For the friction material analysis, sample X, the fibres were extracted from the sample, as they cannot be crushed. They will have therefore no influence on the DTA–TG analysis. Furthermore ethanol was added to the sample crushed in order to obtain a homogeneous paste and avoid separation between particles (10% in mass of ethanol). The evaporation of the ethanol at the beginning of the experiment (below 100°C) was deduced and therefore does not appear on the results. The zero of the curve for the change in mass is fixed after the evaporation of ethanol. This is possible as there should not be any reaction in sample X at that temperature during this experiment as the possible reaction will have already taken place during the curing cycle (the curing temperature is higher that 100°C).

A few samples of X were cut from the brake pad (using hand sawing to avoid any important increase in temperature, which could deteriorate the sample), and analysed directly as a small block. The small block had a size of approximately 3×3×5 mm. The thermal analyses DTA–TG were made at Risø National Laboratory using a Netzsch Simultan TA. The heating rate used was +2°C min^{-1} up to different temperature T and cooled down with a cooling rate of –10°C min^{-1} from the defined T to 25°C. The samples were named X-T, where T corresponds to the temperature reached. The blocks were polished with a silicon carbide disc up to 1000 μm and analysed with SEM GSM 840, connected to EDS Noran Voyager, which allowed the differentiation between the different phases.

Results and discussion

The analysis of sample X

Figure 2 shows a total mass loss at 1000°C of 4% for sample X. This total mass loss corresponds to several mass losses and mass gains accompanied by exothermic peaks between 250 and 850°C. Below 100°C the evaporation of ethanol takes place. Between 265 and 460°C there is a decrease in mass of around 4%. A large exothermic peak accompanies this process. Between 460 and 720°C another decrease in mass of around 5% takes place, also accompanied by a large exothermic peak. Between 720 and 800°C, a large exothermic peak accompanies an increase in mass of 2%. At around 800°C a very quick and rather large mass gain of 2.5% is accompanied by a very narrow exothermic peak. The decomposition reaction ends at around 825°C.
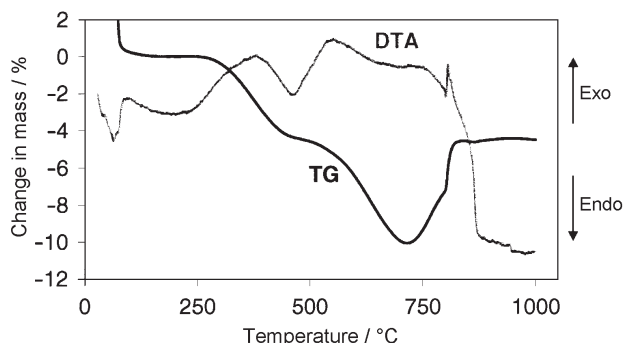
Fig. 2 DTA–TG curve of sample X, a semi-metallic friction material

A mass gain accompanied by an exothermic peak is a signature of an oxidation [5]. A mass loss accompanied by an exothermic peak can also be an oxidation, but the compound formed is a gas (combustion). The decomposition of the binder should be seen as a mass loss.

Therefore the two mass losses accompanied by exothermic peak could be the combustion of carbon and the decomposition of the binder. The mass gain could correspond to the oxidation of iron. The combustion of carbon should correspond to a mass loss of around 40% (from the amount of carbon in the sample), and the maximum mass loss of sample X is around 10%. Therefore the reactions overlap, and the oxidation of iron has already started before the visible gain in mass. It is impossible to see distinctively the decomposition of the binder system. Other measurements are necessary in order to understand the thermal behaviour of sample X.

The combustion of carbon releases gases. This release is accompanied by a mass loss, which, itself, can be partly detected by DTA–TG (overlapping of reactions) [5]. It became interesting to couple the thermal technique with a system for detecting the gas evolved. For example, the detection of carbon dioxide should show more precisely when the combustion of carbon takes place.

Mass spectrometry

The data from two of the gases were particularly interesting and gave a better understanding of the thermal behaviour of sample X. The gases were CO_2 and H_2O (the analysis of O_2 just confirmed the results). Figure 3 shows the variation of these two gases for sample X and the DTA–TG curves in parallel.

The emanation of H_2O takes place at 75°C (narrow peak) and is also visible between 200 and 450°C (flat peak). The emanation of CO_2 also takes place at 75°C (narrow peak). Then the emanation of CO_2 takes place in 3 steps: between 200 and 475°C, between 475 and 800°C and between 800 and 850°C. At 800°C, the emanation of CO_2 suddenly becomes less important.

The first peak, which appears for the emanation of CO_2 and H_2O, corresponds to a decrease in mass of the sample, and an endothermic peak. The emanation of water
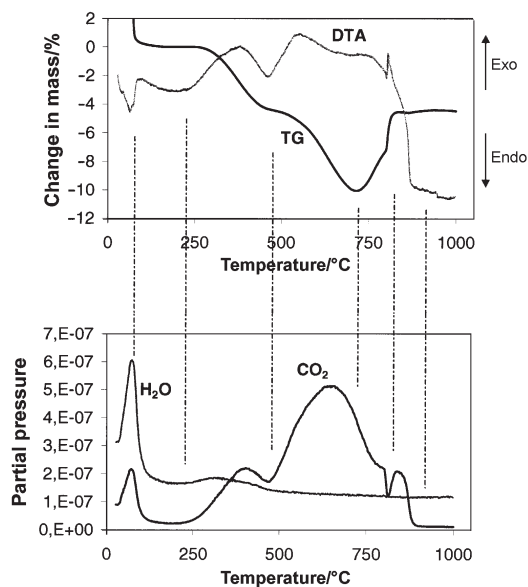
Fig. 3 Combination of DTA–TG and EGA for the semi-metallic friction material

from 230 and 450°C corresponds to a mass loss. The first emanation of CO_2 at low temperature corresponds exactly to an exothermic peak of the thermal analysis and it is accompanied by a decrease in mass. When the emanation of CO_2 decreases, there is a stagnation of the mass. The second emanation of CO_2 corresponds to the second large exothermic peak with a mass loss. This emanation of CO_2 suddenly stops at around 800°C and this corresponds to the very narrow exothermic peak and an important increase in mass.

The evaporation of ethanol used to prepare the sample takes place below 100°C. It is seen as an endothermic peak and a mass loss accompanied by an emanation of water and carbon dioxide.

The emanation of H_2O should mainly correspond to the decomposition of the binder. Therefore the binder decomposes between 230 and 450°C. The curve showing emanation of CO_2 around these temperatures does not have the same shape than the one for H_2O. Therefore, the emanation of CO_2 is also due to the combustion of carbon. The combustion of carbon seems to take place between 250 and 850°C with a slowing down at around 450 and a short stop at around 800°C.

The detection of the gases released did not give any information concerning the oxidation of iron and did not show any differences between coal and graphite. The two mass losses cannot be due respectively to the coal and the graphite (or vice versa), as the mass losses do not correspond to any appropriate amount. Therefore the raw materials were analysed separately.

Analysis of the raw materials

Figure 4 shows the thermal behaviour of iron powder. It is one of the most important additives and varies a lot from one powder to another one, according to the method of production [6]. An increase in mass of 43% is observed between 400 and 900°C and is accompanied by two exothermic peaks (500 and 650°C). This corresponds to the oxidation of Fe into Fe_2O_3 (theoretical mass gain of 42.8%). The evolved gas analysis shows that the partial pressure of O_2 is generally lower at these temperatures, confirming the oxidation hypothesis.
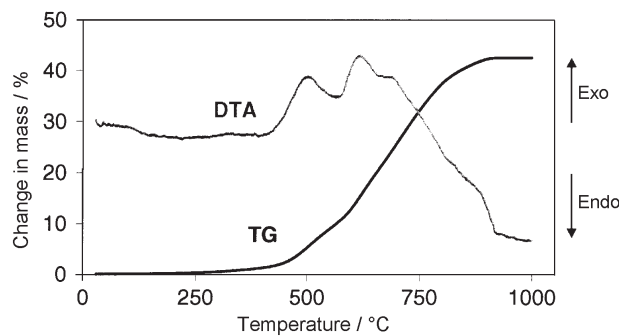
Fig. 4 DTA and TG curves of iron powder

The iron powder oxidised continuously, whereas, when it is inside sample X, the oxidation takes place continuously before 800°C, but it ends very suddenly at that temperature (very narrow exothermic peak). Therefore it seems that either carbon may oxidise preferentially before iron and as a consequence slow down the oxidation of iron or that a corrosion protection may be formed on the surface of the iron particles.

Coal is formed by the decomposition of plants under the action of heat and pressure in the absence of air [7]. As a natural product, it has an extremely varied composition and thus requires analysis itself. Figure 5 shows the combustion of the coal
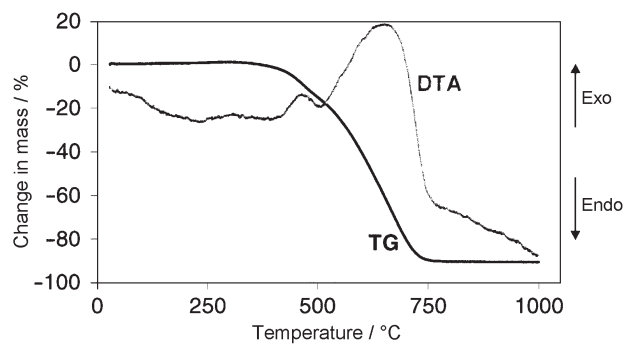

Fig. 5 DTA and TG curves of coal powder

used for sample X. It combusts between 400 and 700°C to leave ash (mass loss of 92%). This combustion corresponds to two exothermic peaks which respectively start at 420 and 460°C. These two steps in the combustion are also obvious on the evolved gas analysis (Fig. 6) with a variation in the emanation of CO_2. The coal contains a little water. The partial pressure of H_2O increases at 300 and 450°C. The water content must be small, as no corresponding mass loss can be detected on the TG curve.
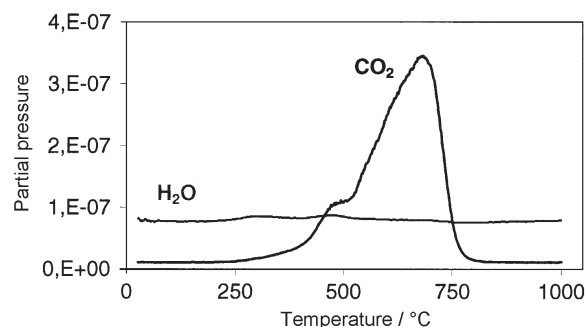

Fig. 6 Emanation of CO_2 and H_2O for the coal powder

Graphite is a medium temperature lubricant [4]. It also combusted with a mass loss of 98%, but in one-step between 600 and 850°C (Fig. 7). The partial pressure of CO_2 increases between these temperatures while for O_2 it decreases. No emanation of water can be detected.
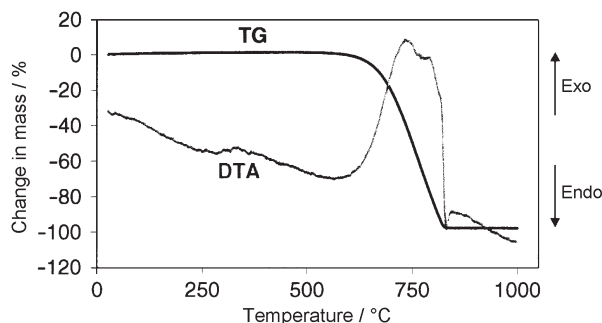

Fig. 7 DTA and TG curves of graphite powder

None of these raw materials underwent any curing treatment, but all the reactions mentioned actually take place at a temperature that is higher than sample X curing temperature. Therefore the corresponding reactions should also be detected in the analysis of the sample X.

The binder partially decomposes (Fig. 8) between 250 and 450°C. It corresponds to a mass loss of 33% of binder (the quantity of quartz is not taking into account in this calculation). It has to be noted that the binder would have already decomposed during the curing, however the binder inside sample X would also have already de-
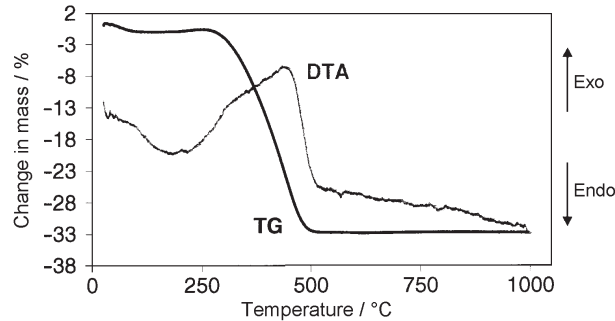
Fig. 8 DTA and TG curves of binder system

composed during the curing. So the decomposition of the binder should be similar to
that inside sample X, unless the binder is more stable within this other environment.

Coal decomposes before graphite. The first mass loss on sample X curve could
correspond to the binder system decomposition and the first oxidation of coal (which
is fairly small). The second decomposition of the coal takes place between 500 and
700°C. The graphite only combusts between 600 and 850°C. The localisation of the
oxidation of iron is still not very clear, as the presence of carbon slows it down.

Optical analysis at different temperatures

Figure 9 shows the DTA–TG analysis of sample X as a block at 1200°C. The curve is
rather similar to the curve obtained for sample X analysed as a powder. Differences in the
mass gain and loss can be explained by a lack of homogeneity (the blocks are fairly
small, and the particles fairly big, therefore a block might contain more or less of each
raw materials). The reactions can have different starting temperatures, as the environ-
ment is different. These differences must be taken into account, but they are not impor-
tant and therefore the results obtained with optical analysis on blocks at different temper-
atures can be used for explaining the thermal behaviour of sample X as a powder.
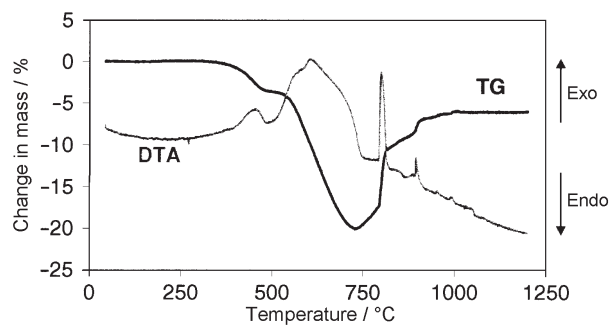

Fig. 9 DTA and TG curves of sample X as a block

Figure 10 shows sample X before and after curing at 1200°C. At high temperatures the carbon is gone, and the iron forms with the fibres a solid network.
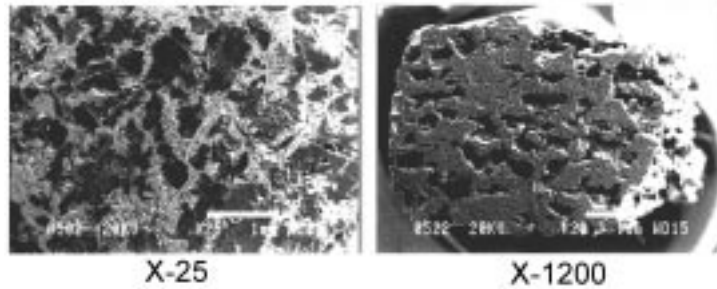

Fig. 10 Visual aspect of sample X as a block before and after a curing cycle at 1200°C

Figure 11 shows that the oxidation of iron and fibres starts on the surface of the particles. The sample analysed is X-560, and no oxidation of the iron has been detected before (previous analysis at 530°C). Therefore the oxidation of iron really starts at around 550°C (in the block).The distinction between the iron oxidised and the iron non-oxidised, as well as the fibres oxidised and non-oxidised is very easy with the SEM (Fig. 12).

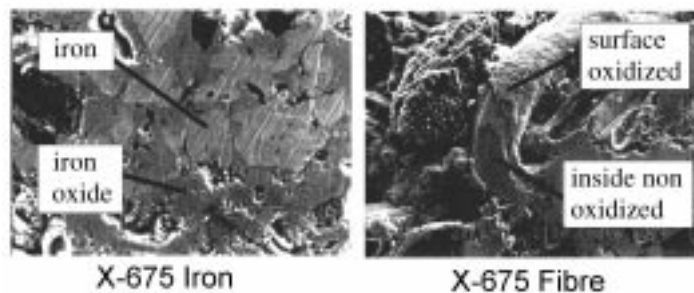**Fig. 11** Visual aspect at the beginning of the iron oxidation at 560°C

Fig. 12 Visual aspect of the oxidation of iron and fibres at 675°C

Below 800°C, a fairly large amount of iron and fibres is still not oxidised. At 850°C, the iron phase and the fibres are all completely oxidised.

The iron and the fibres oxidised continuously from the surface to the centre of the particles from 500 to 800°C, with a quick oxidation at the end of this temperature range.

Conclusions

To summarise the results, Fig. 13 presents all the reactions on the DTA–TG curves that occurred during the increase in temperature of sample X.
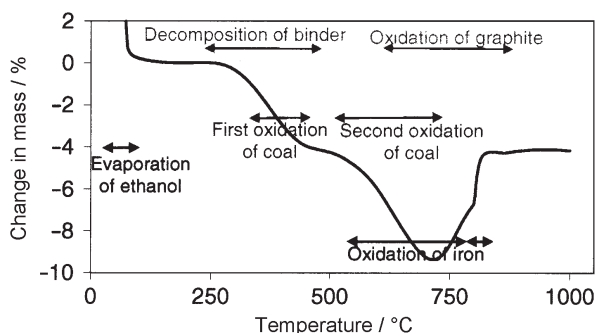

Fig. 13 Thermal behaviour of a semi-metallic friction material

The first reaction before 100°C corresponds to the evaporation of ethanol added during the preparation of the sample.

The decomposition of the binder system takes place between 250 and 475°C. The localisation of this reaction has been found using mass spectrometry (main component that emanated water).

The oxidation of the coal occurs in two steps. The first oxidation starts at around 300 (the same temperature as the raw material by itself) and ends at around 475°C. The second oxidation of the coal takes place between 525 and 700°C (increase in mass). The separation of the two oxidation steps of the coal is more significant in sample X than in the raw material itself. This can be due to the fact that the first oxidation of iron starts in between.

The oxidation of the graphite takes place between 600 (more stable than the coal) and 850°C. There is every indication that the oxidation continues above 800°C (deducted from a slight decrease in mass above 800°C, and the analysis of the raw material).

The oxidation of the iron within sample X occurs in two steps whereas the analysis of the raw material shows a continuous oxidation of the iron. This is due to the carbon oxidised preferentially before the iron or the formation of a corrosion protection on the surface of the iron particles. The oxidation of iron starts at around 500 and continues slowly until 800°C when it becomes very fast.

This work, using combined techniques, gave a new knowledge and a better understanding of the chemical-physical decomposition processes that occur when a friction material is exposed to severe thermal conditions.

It enables the development of new products with promising properties and particularly for brake pads that are stable at high temperature.

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