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Thermal and microchemical investigation of automotive brake pad wear residues

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Abstract

By means of the combined use of simultaneous differential thermal analysis and thermogravimetry (DTA–TG) and scanning electron microscopy + energy dispersive spectrometry (SEM + EDS), the thermal and microchemical investigation of an automotive wear brake pad and its residues produced during the long service of a largely used Italian car, is carried out. The wear residues are produced during braking as the pad releases microscopic debris from the contact surface due to the combination of friction induced heat and mechanical actions such as attrition and wear. The results of SEM + EDS characterisation combined with the results of the thermal behaviour study, show the chemical and physical changes induced in the microchemical structure of the pad during braking and further, allow to measure the surface contact temperature at the interface between brake pad and metallic counter-face that does not exceed 720 °C.
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1. Introduction

The friction and wear behaviours of automotive brake pads are very complex to predict being dependent on various parameters such as microchemical structure of the pad and of the metallic counter-face, rotating speed, pressure and contact surface temperature [1]. This latter value could largely vary and some authors [1,2] have reported different estimated values for the maximum contact surface temperature, ranging from 600 to 1500 °C at the interface between the automotive brake pad and the metallic counter-face. In order to have good and stable brake performances as a function of the temperature, this latter parameter should be measured as precise as possible in order to tailor the chemical and physical structure of the pad because if temperature reaches extreme conditions, wear rate increases and friction decreases dramatically.

There are several types of automotive car brake pads that contain different organic and inorganic compounds such as metal sulphides such as Sb_2S_3, abrasives such as silica or alumina, fillers such as silicates and sulphates generally of barium, metal particles, carbon fibres, solid lubricants such as graphite, phenolic resin binder and more rarely different kinds of rubber, in different combinations and whose exact formulation could be unknown [1,3]. During braking, the brake pad releases microscopic residues from the contact surface between the pad and the cast iron or steel disks that act as counterparts. The main chemical–physical reactions occurring during braking are due to the combination of the friction induced heat and mechanical actions such as attrition and wear. The microchemical structure of these pulverised and blunt particles depends on various experimental parameters such as rubbing speed and pressure as well as on the contact surface temperature and on pad microchemical structure but only very little is known about what really happens during braking at the contact surface [3] and in particular, the value of maximum surface temperature has been never exactly measured.

By means of the combined use of simultaneous differential thermal analysis and thermogravimetry (DTA–TG) and scanning electron microscopy + energy dispersive spectrometry (SEM + EDS), the thermal and microchemical

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investigation of the brake pad and its wear residues produced during the long service of a largely used Italian car is carried out. In particular, the microchemical structure and the thermal behaviour of the brake pad and its wear residues are studied in air in order to evidence the chemical and physical changes suffered by the combination of heat and mechanical actions and to estimate the brake pad contact surface temperature.

2. Experimental

DTA–TG simultaneous measurements were carried out in air, from room temperature to 1400 °C for wear pad and its residues and to 1100 °C for stibnite (Sb_2S_3) using an automated thermal analyser (Stanton Redcroft STA-781) computer controlled. Cylindrical alumina crucibles of diameter 4 mm and depth 2 mm were used. Approximately 5–10 mg of sample was heated in air at a heating rate of 20 °C min^{-1}. The Sb_2S_3 sample of about 10 mg was obtained from a pure stibnite (Sb_2S_3) crystal.

The brake pad examined in this study is a pad made to fit a Fiat Punto car that is a widely used car in Italy. Its wear residues have been sampled inside the braking equipment.

Because, the large size distribution of particles dispersed in the carbon matrix could be a problem in the comparison between size particles of Sb_2S_3 in the brake pad and in the wear residues during microchemical and micromorphological characterisation, flat cross-sections for brake pad and wear residues have been prepared by embedding them in a resin and by metallographically polishing with carborundum papers and diamond pastes up to 0.10 μm in order to have mirror like surfaces. This preparation method combined with the SEM observation using back scattered electrons allows to better compare the particle size and to study the chemical nature of the wear residues and the brake pad constituents and therefore, in this way it is possible to ascertain chemical and size variations induced during braking.

Scanning electron microscopy + energy dispersive spectrometry (SEM + EDS) characterisation was carried out by using a Leo Cambridge 360 scanning electron microscope equipped with an EDS apparatus, a four sector back scattered electron detectors and a LaB_6 filament. The sample has been coated with a thin layer of carbon (about 3.0 nm) in order to observe the wear residues without charging effects.

3. Results and discussion

In Fig. 1, the microchemical structure of the brake pad in as received (a.r.) condition is shown by scanning electron microscopy (SEM) back scattered (BS) images taken both at low and higher magnification, micrographs 1 and 2, respectively. The energy dispersive spectrometry (EDS) results illustrate the elemental chemical composition of some different inorganic phases that constitute the brake pad. In particular, the presence of barium, sulphur and antimony and sulphur containing particles [1,3], whose size ranges from 7 to about 10 μm, is evidenced with also the presence of metal-based particles (Cu, Fe) in different amount and embedded in the carbon-based matrix that appear as dark regions in the micrographs.

In Fig. 2, the microchemical structure and the micromorphology of the brake pad wear debris in as collected (a.c.) conditions are shown by a SEM BS image with EDS results (spectrum A–F) that evidence the elemental chemical composition of some different inorganic phases that constitute the brake pad wear residues. The EDS data show the presence of small abrasive alumina particles and of iron and copper compounds in different amount. Furthermore, EDS results evidence the presence of barium sulphate (not shown) and antimony sulphide particles with a S/Sb atomic ratio of 1.5 as already observed in the pad brake in a.r. condition. The only one difference with respect to the virgin product is the size of the Sb_2S_3 particles that in the wear residues is noticeably reduced to about 2–3 μm.

In order to better evidence the microchemical structure of the brake pad wear residues, a cross-section has been produced and it is shown in Fig. 3 by a SEM BS image with ED spectra (spectrum A–D). These results clearly confirm the different elemental chemical composition of the inorganic phases that constitute the brake pad wear debris. Iron enriched particles coming also from the cast iron or steel (iron-based alloy) disks counterparts are present with a small amount of copper and zinc with silicon, antimony, sulphur, barium and aluminium very small enriched particles whose size is ranging from 3 μm to sub-micron dimension. Also in this case, when only antimony and sulphur have been detected, a S/Sb atomic ratio of 1.5 has been measured via quantitative EDS analysis as already observed in the pad brake in a.r. condition. It is worth noting that we have never observed in this material lead enriched particles as reported by other authors [2] that have studied the brake lining debris.

The observation of the cross-sectioned particles indicate that the braking action has only reduced the size of the inorganic pad constituents and blunt them. Indeed, by comparing the microchemical structure of the virgin pad and its wear residues it is possible to evidence that the combined action of wear and friction have ground and pulverised the inorganic components of the pad and the resulting particles still have the chemical composition and physical structure of the phases present in the virgin pad [1,3] but the grain size is reduced up to a micron or sub-micron dimension. These results reveal that only size changes occur for the inorganic constituents during braking at the surface of the brake pad material and that only a mix of all inorganic compounds of the pad is formed during braking.

Furthermore, the SEM + EDS investigation has evidenced in the virgin pad and in the pad wear residues, that sulphur is bonded with antimony or barium thus forming antimony sulphide or barium sulphate, respectively, and that the wear and friction actions have induced a grinding and a physical
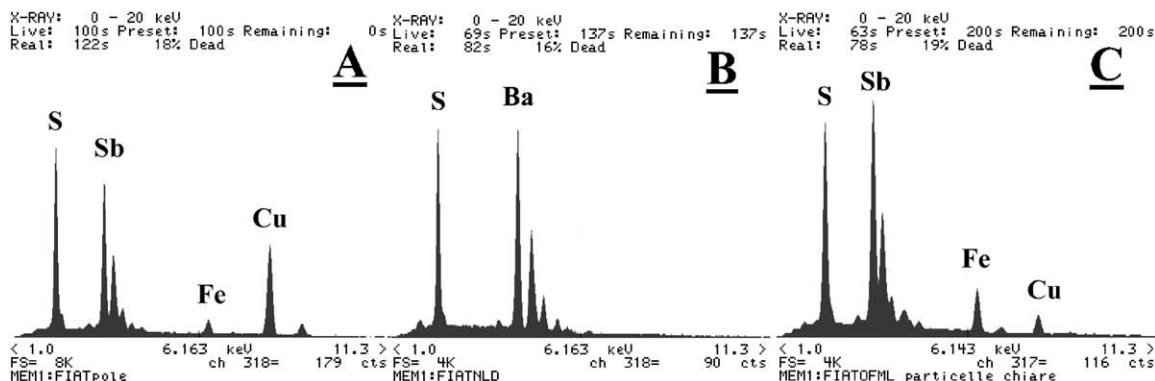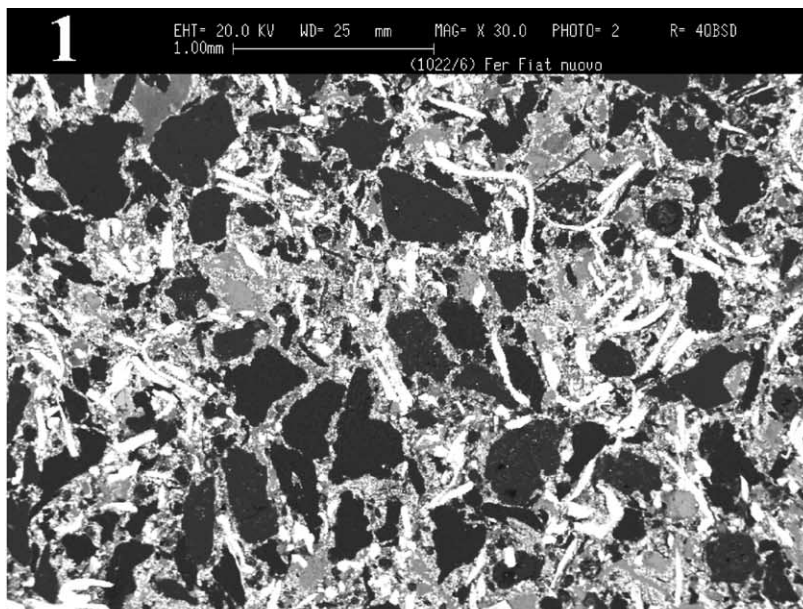
Fig. 1. Scanning electron microscopy (SEM) back scattered (BS) images at low and higher magnification, micrographs 1 and 2, respectively, show the microchemical structure of the automotive brake pad. The energy dispersive spectrometry (EDS) results (spectrum A–C) illustrate the elemental chemical composition of some different inorganic phases of the pad embedded in the carbon-based matrix that appear as dark regions in the micrographs.
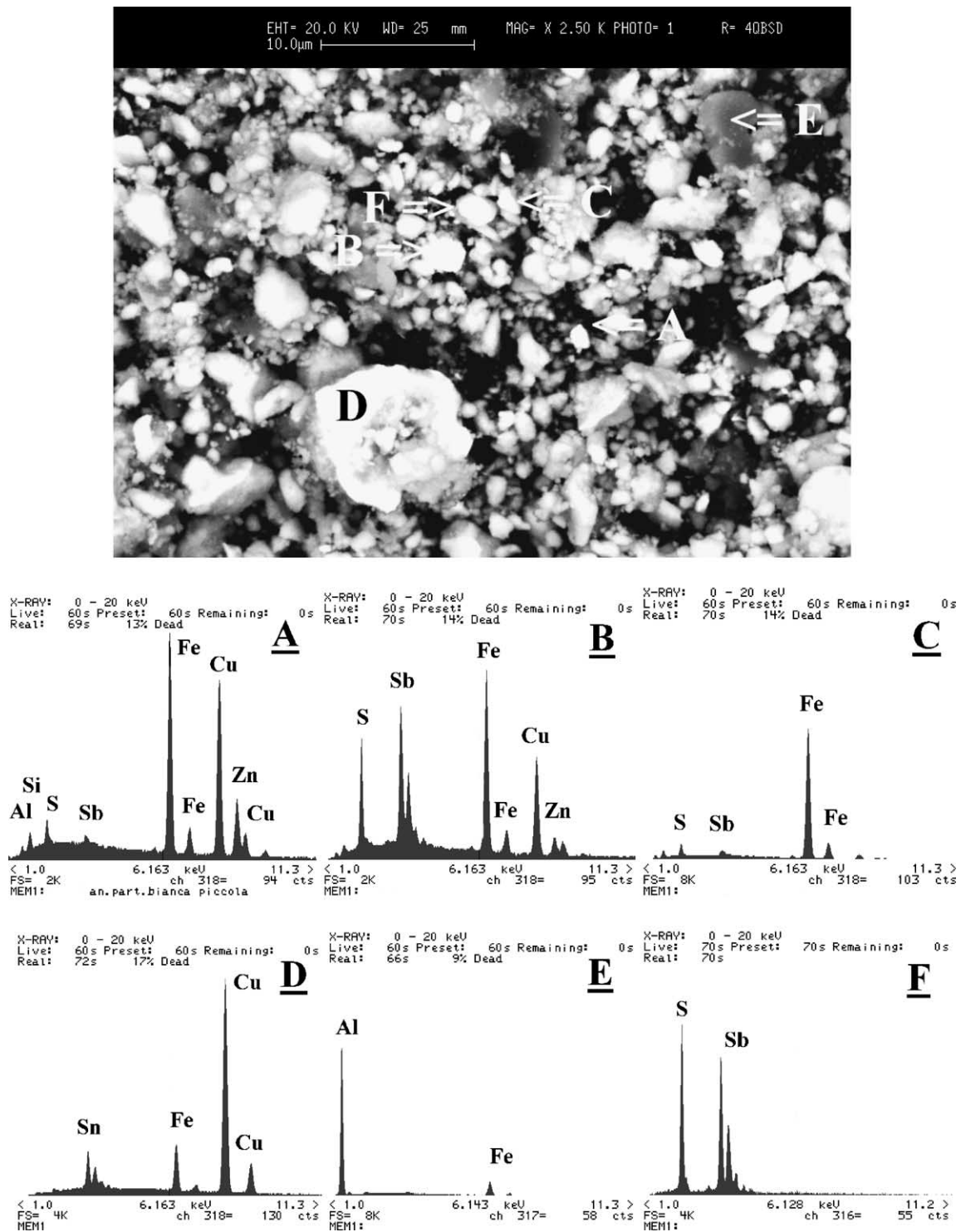
Fig. 2. Microchemical structure and the micromorphology of the automotive brake pad wear residues in as collected (a.c.) conditions. The EDS results (spectrum A–F) evidence the elemental chemical composition of some different inorganic phases that constitute the brake pad wear residues.

blending of the inorganic constituents and likely of the organic compounds and not chemical bonding changes. Indeed, on the base of SEM + EDS results, the presence of phases characterised by the contemporaneous presence of sulphur, barium and antimony or the elemental presence of

only antimony, barium or sulphur has been never observed for this widely used Italian brake pad.

For what concerns the chemical or physical changes occurring to the organic constituents of the brake pad during braking, simultaneous DTA–TG analysis has been
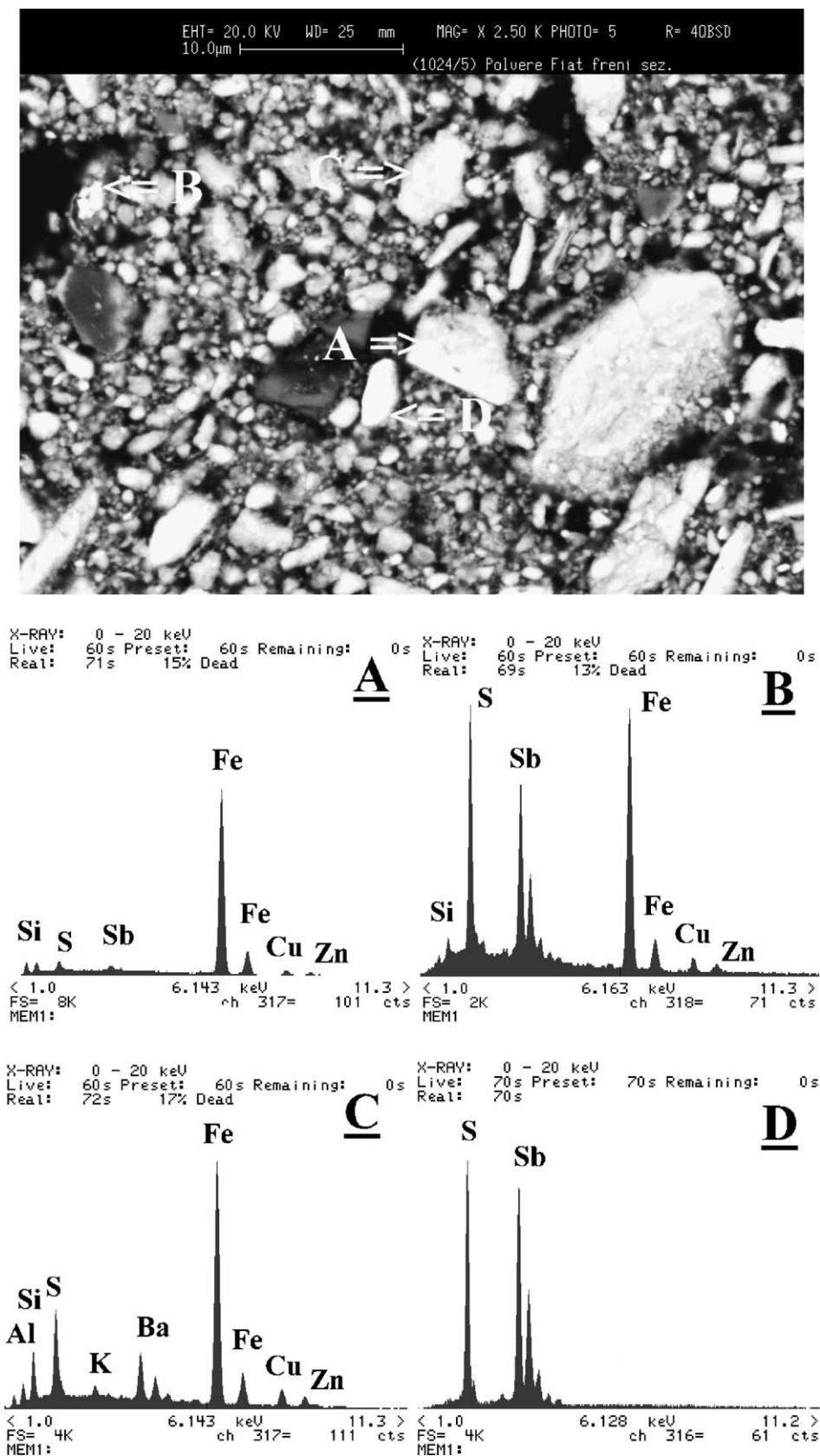
Fig. 3. SEM BS image that shows the cross-sectioned microchemical structure of the automotive brake pad wear residues. The EDS results (spectrum A–D) evidence the elemental chemical composition of some different inorganic phases that constitute the brake pad wear residues.
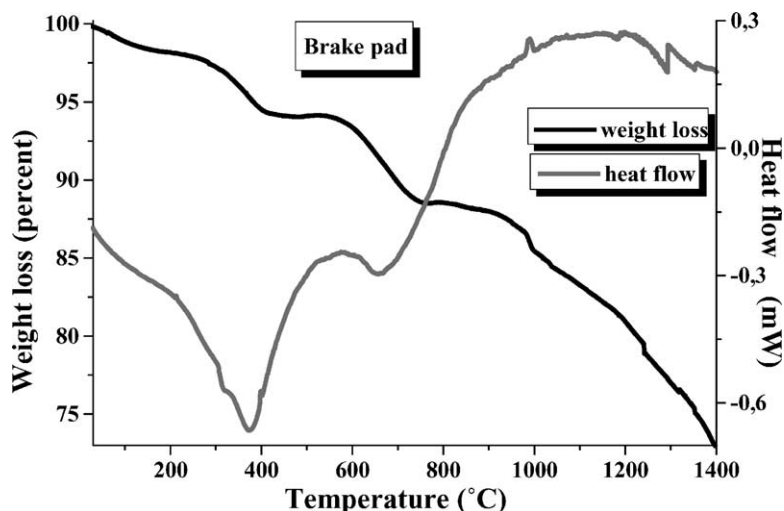
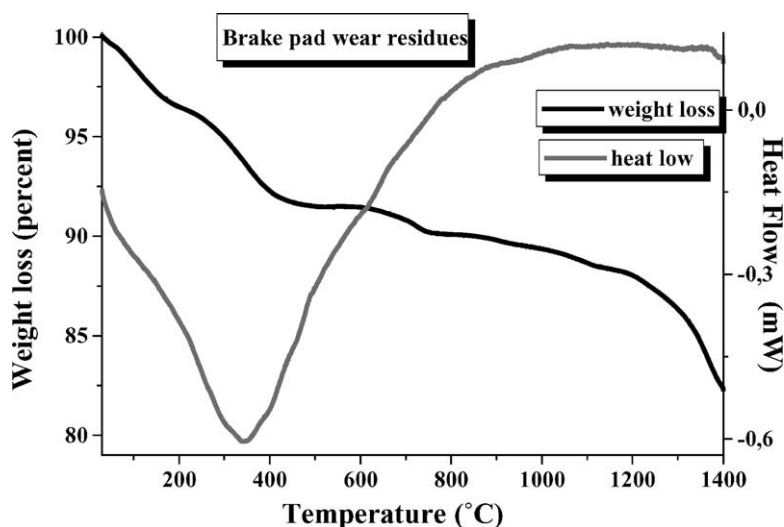Fig. 4. DTA–TG curves for the automotive brake pad in air (heating rate $20\,^\circ\mathrm{C\,min^{-1}}$).

Fig. 5. DTA–TG curves for the automotive brake pad wear residues in air (heating rate $20\,^\circ\mathrm{C\,min^{-1}}$, particle size ranging from $10\,\mu\mathrm{m}$ to $< 1\,\mu\mathrm{m}$).

carried out for the brake pad in a.r. condition and for the wear residues and in Figs. 4 and 5, the thermal curves are reported, respectively.

The thermal traces for the brake pad in a.r. condition and for its wear residues show a broad exothermic drift in the temperature range ranging from 50 to $200\,^\circ\mathrm{C}$ with an associated weight loss of about 2–3% likely due to the oxidation or evaporation of organic compounds. At about 350–$370\,^\circ\mathrm{C}$ another wide exothermic peak is present with a heavier weight loss of about 5% for both samples. Also in this case the exothermic peak is probably due to the oxidation of brake pad organic constituents because the inorganic constituents of the brake pad do not suffer of any relevant chemical or physical changes in this temperature region. At higher temperatures, by comparing the DTA–TG curves, it is possible to evidence that the brake pad shows a wide exothermic signal peaked at about 670–$700\,^\circ\mathrm{C}$ with an associated weight loss of about 7% while the DTA–TG curves for the wear residues show a very small and broad exothermic peak with an associated weight loss of about 2%. At temperature higher than $800\,^\circ\mathrm{C}$ and up to $1400\,^\circ\mathrm{C}$ the thermal behaviour of the brake pad and its wear residues are similar.

These latter thermal data seems to evidence comparable behaviours of the brake pad and its wear residues, the only main difference between their thermal properties is the lower exothermic contribution of the wear residues with respect to the virgin in the temperature range from 550 to $720\,^\circ\mathrm{C}$. These data suggest that the major amount of wear residues are produced by the wear induced grinding at the contact surface that pulverises the brake pad causing only a size reduction of the organic and inorganic constituents and maintaining unchanged their chemical nature. Only a small fraction of the wear residues are also affected by the combination of friction induced heat and mechanical actions that changes the chemical nature of some organic compounds. Furthermore, on the base of these information it is possible
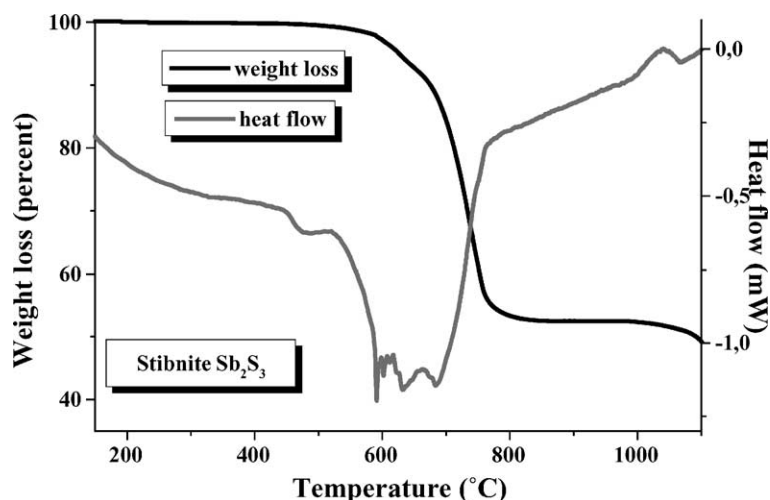
Fig. 6. DTA–TG curves for stibnite (Sb_2S_3) in air (heating rate $20\,°C\,min^{-1}$, the Sb_2S_3 sample of about 10 mg was obtained from a pure stibnite crystal).

to suggest that the maximum contact surface temperature reached during braking does not exceed $720\,°C$.

In order to confirm the value of the maximum surface temperature reached at the interface between the pad and the metallic counter-face and considering that antimony sulphide is present in the brake pad and in its wear residues as Sb_2S_3, we have studied the thermal properties of stibnite in air. Indeed, antimony sulphide and its thermal decomposition temperature could be considered as an indicator of the maximum reached temperature during braking because the thermal behaviour of mineral sulphides [4,5] show in the temperature range from 600 to $750\,°C$ various reactions such as oxidation, decomposition or ignition that dramatically change their chemical and physical structure.

The DTA–TG curves for Sb_2S_3 are shown in Fig. 6. The results evidence the presence of a small and broad exothermic peak at about $460\,°C$ without any noticeable weight variation that has been interpreted by Madkour [6] as the surface oxidation of stibnite first to Sb_2O_4 and then Sb_2O_3 that is stable up to $570\,°C$. At this temperature a phase change of Sb_2S_3 occurs corresponding to another solid form with a polymeric structure [6] which has no associated mass loss. As already observed by Dunn and coworkers [4,5] for other mineral sulphides, the thin oxide coating formed on the stibnite crystal can be quite protective and inhibits the diffusion of oxygen to the unreacted sulphide and this temporary inhibition and the dynamic heating within the protective coating can give rise to the decomposition of the antimony sulphide [4,5]. As shown in Fig. 6, the thermal curves for Sb_2S_3 in the temperature range between $550\,°C$ and $730\,°C$ are quite complex and governed by the formation of the oxide/sulphate layers on stibnite and its breakdown that influence the further chemical reactions. This behaviour is evidenced also by additional features observed in the DTA curve that appear as sharp exothermic signals which precede the main exothermic peak. These latter have been attributed to a number of causes which include a periodic cracking of

the protective coating which expose fresh sulphide for oxidation [4,5]. From the DTA trace shown in Fig. 6, it is possible to state that thermal decomposition of stibnite starts at about $530\,°C$ and is complete at about $750\,°C$. Therefore, the brake pad surface maximum temperature does not exceed normally this temperature value because we have observed in the wear brake pad debris only stibnite particles with a Sb/S atomic ratio of 1.5 and not the elemental presence of antimony without sulphur or with an atomic ratio lower than 1.5.

The SEM + EDS and DTA–TG results indicate that the major wear consequence [3] is the grinding of inorganic and organic constituents and that the organic binder change partially also its chemical nature during the asperity heating induced during braking. The above reported results seem to confirm the hypothesis proposed by other authors [3] that during braking small contact plateaus [7] are formed at the contact surface by the harder brake pad constituents that give rise to the formation of a thin layer which differs in composition and structure from the mating parts of the brake system and will constitute the major part of the wear residues. This thin surface layer is a mixture of the products of the tribo-oxidation reaction [7], of the ground brake pad constituents and debris of the counterpart material. Indeed, SEM + EDS and DTA–TG results indicate that the organic fraction of the brake pad has been ground to a sub-micron dimension and also partially changed from a chemical point of view due to the effect of the asperity heating. Furthermore, DTA–TG results suggest only a little fraction of the organic constituents is subjected to the tribo-oxidation reactions likely only the fraction that is produced where more severe conditions are present.

These information could be useful for the optimisation of the brake system performances or for the development of new friction materials that till now has been done only empirically [3] starting from well known base composition which have been modified by adding different additives and testing them without any relevant chemical–physical investigation.

Indeed, usually, during standard brake testing, wear rate and brake pad performance trends are determined without investigating the mechanisms responsible for these trends [8,9].

4. Conclusions

By means of the combined use of differential thermal analysis and thermogravimetry (DTA–TG) and scanning electron microscopy + energy dispersive spectrometry (SEM + EDS) the thermal and microchemical investigation of automotive wear brake pad and its residues produced during the long service of a largely used Italian car is carried out.

The results show the complex microchemical structure of the brake pad and its wear residues and indicate that the maximum contact surface temperature reached during braking does not exceed 720 °C. Furthermore, SEM + EDS results show that the major wear consequence is the grinding of inorganic and organic constituents of the brake pad. These latter change partially also their chemical nature due to the asperity heating induced during braking.

These thermal and microchemical information could be useful for obtaining a through understanding of the wear mechanism and the chemical changes suffered by the brake pad materials to be used for the improvement of their durability and efficiency.

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