

Quantitative EDS phase maps for the analysis of complex ceramic composites

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Complex composite materials are carefully engineered on the microscale in order to deliver a specific macro-level performance. Understanding the chemical composition on the microscale is therefore crucial to developing next generation composites and to quality monitoring of current generation composites. Scanning Electron Microscopes equipped with Energy Dispersive Spectroscopy x-ray analysers are well-positioned for this type of micro-scale analysis. The results, however, are qualitative and prone to analytical user bias. A new technique is presented here that generates quantitative elemental phase maps with no user bias and, in fact, no user input except for the raw data. This technique is used here to analyse and compare the underlying chemistries of a semi-metallic and a ceramic brake pad and the macro level performance of the two brake pads.

Introduction

Brake pads are a critical part of a vehicle's overall braking system. With the broad diversity of available brake pad types, sub-types and unique chemistries there is an open question as to which brake pad provides the best overall performance.

First and foremost, braking is a tradeoff. A brake pad that works well in the stop and go traffic of a busy city is not suitable for performance racetrack driving. Similarly, a dedicated pad for off-road, heavy-duty work will not meet the sociability needs of a quiet neighborhood. There will never be one perfect brake pad chemistry for every type of vehicle or in every situation. Clean, quiet stops are traded for reduced braking performance. Greater braking performance is generally traded for a short pad life. A longer pad life may come at the expense of added wear on the rotor or reduced braking.

The one consistent truism is that brake pad chemistries are evolving rapidly and every category of braking performance is improving across all fronts. Much of this evolution is driven by advances in materials characterisation techniques such as Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS). SEM-EDS offers a unique and effective view of the material composition on the sub-micron scale. An improved understanding and monitoring of the sub-micron composition of materials directly translates into improvements in performance and in manufacturing control on the macro scale [1-4].

Experimental

Two different styles of brake pads were analysed. Both pads were non-Original Equipment Manufacturer (OEM), aftermarket parts that were taken from Dodge Grand caravan minivan after 18,000 miles of wear. One pad was ceramic and advertised as: a quiet, sociable pad with effective stopping power in all conditions. The second pad was a semi-metallic advertised as: designed for pursuit vehicles with advanced formulation for superior stopping power.

Electron images were collected using a JEOL JSM-7001F scanning electron microscope (SEM). Energy Dispersive Spectroscopy (EDS) was used for elemental analysis. The EDS x-ray spectral imaging data sets were collected with a Thermo Scientific™ UltraDry™ EDS detector running on the Pathfinder software platform.

The back story on brake pads

There are several important characteristics in considering a brake pad material:

- Stopping power: friction of the pad
- Brake pad life vs. stopping power vs. wear to the rotor
- Sociability: braking noise & brake dust generation
- The ability of the material to provide smooth, even contact with the rotor or drum
- The materials ability to resist brake fade at increased temperatures
- The ability to dissipate heat and to avoid warping of the pad or the rotor
- Manufacturability and cost

Types of brake pads:

Asbestos: Up until the 1970s, straightforward asbestos was viewed as having an optimal performance in all categories. As the serious health-related hazards of asbestos became apparent, it became imperative to develop alternate materials.

Non-metallic materials: Non-metallic organic brake pads replaced asbestos-containing pads in the early 1970s. These are made from a combination of various synthetic substances bonded into a composite, principally in the form of cellulose, aramid, PAN, and sintered glass. While gentle on rotors, they produce more dust and have a short service life.

Fully metallic materials: These pads, composed of sintered steel without any synthetic additives, are used only in racing vehicles. They are very long-lasting, but require even more force to slow a

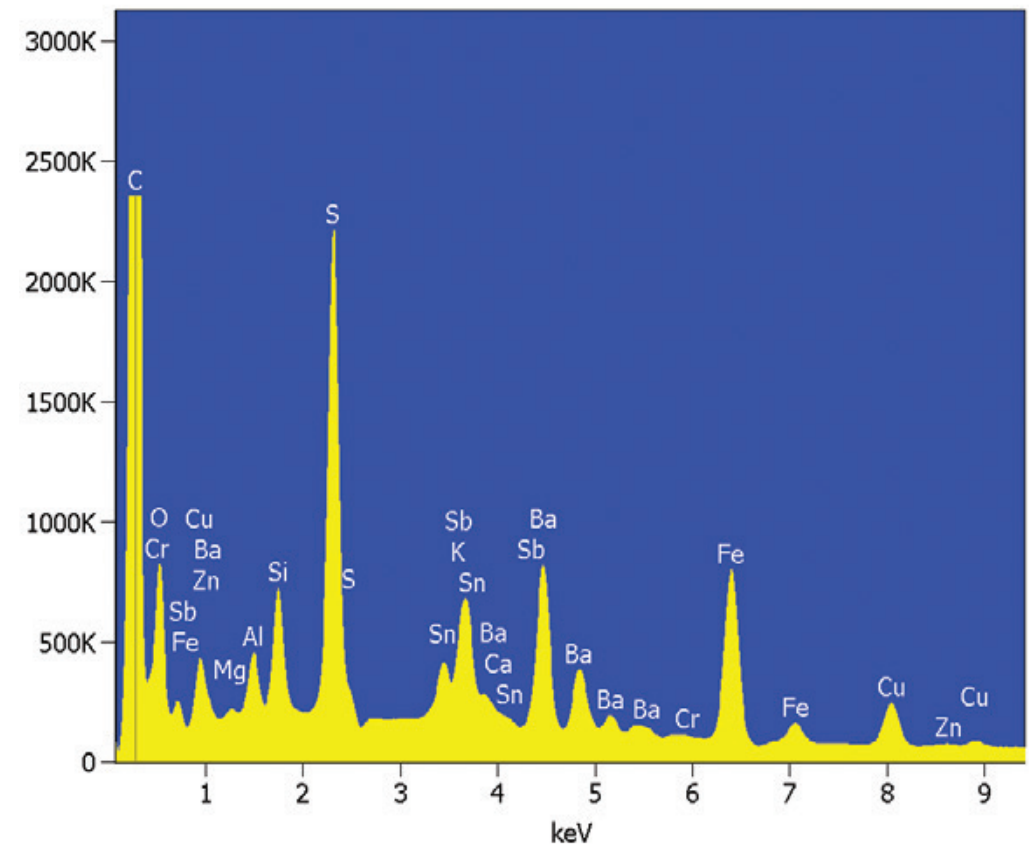


Figure 1. Overall EDS spectrum from the ceramic brake pad.

vehicle and are extremely wearing on rotors. They also tend to be very loud.

Semi-metallic materials: Synthetics mixed with some proportion of flaked metals. This type of friction material was developed in the late 1970s and early 1980s. The formulation used far less organic material, and more than half of the composition of the lining was metal particles. This made for a harder pad than the organic type with a much longer life, more fade-resistance and more efficient heat dissipation. The amount of dust was reduced and the stopping power of the brake assembly was increased. The increased hardness of the pad also meant that these advantages came at the expense of both increased noise and increased wear to the (more expensive) rotors, which now had to be replaced more often.

Ceramic materials were introduced commercially in the mid- to late 1980s. Composed of clay and porcelain bonded to copper flakes and filaments, these are a good compromise between the durability of the metal pads and the grip and fade resistance of the synthetic variety. Copper is a good metal for heat dissipation and its softness reduces metal-to-metal wear. Advanced ceramic fibrous materials provide rigidity and heat dissipation, while also absorbing vibration that leads to brake noise. The ceramic material produces very little dust as it wears. The principal drawbacks are that, despite the presence of the copper, ceramic pads generally do not dissipate heat as well as semi-metallic pads. This can eventually cause the pads or other components of the braking system to warp. Ceramics also do not brake as aggressively as semi-metallic, and the ceramic formulation is more expensive than the semi-metallic counterpart.

| Element | %At |
|---------|------|
| O | 23.7 |
| S | 20.4 |
| Fe | 16.9 |
| Ba | 8.6 |
| Si | 7.7 |
| Cu | 6.4 |
| Al | 4.2 |
| Ca | 3.9 |
| Sb | 3 |
| Sn | 2.8 |
| Cr | 1.1 |
| K | 0.7 |
| Zn | 0.4 |
| Mg | 0.3 |

Table 1. Relative concentration (atomic %) of elements present in the ceramic brake pad; carbon excluded.

Current component chemistries within the pads

Matrix: The matrix forms the base composition of the brake pad that creates the form and binding of the overall part. The chemistry is typically carbon-based and fibrous.

Abrasives: Abrasives provide the actual friction which causes the braking. Increasing the amount or effectiveness of the abrasives improves the overall braking performance. The chemistry is typically metallic oxides, mainly Fe- and Cu- based oxides and then also silicates such as SiO₂ (silica or quartz)

and alumina-silicates (AlSiOx). As the base of the pad wears faster than the silicates, these silicates protrude from the base and provide significant bite into the rotor.

Fillers and Stabilizers: The fillers are used for a variety of unique purposes such as increased wear resistance, temperature stability, minimizing fade with temperature or water exposure. Some fillers are also used to provide corrosion resistance, desulfurization of the Fe and Cu or to inhibit the growth of surface layers that degrade performance over time. These chemistries are predominantly barium sulfate, calcium / calcium carbonate / calcite and a variety of other unique, specialty chemistries with a very application-specific purpose in mind.

Lubricants: Lubricants ensure a smooth contact between the pad and the rotor. This reduces noise and dust while improving the overall feel during the braking process. This chemistry can be simple graphite or, more commonly, a metal (Fe-Sb-Mo-Sn-Mn) sulfide.

Even within a single pad type, the specific chemistry of that pad has a significant impact on the performance. A major challenge in the manufacture of automotive brake pads/shoes is controlling the ingredients and distribution of these components. Reproducibility of the formulation and the distribution of the raw materials is the key to obtaining good quality control of the final product. SEM-EDS analysis and the use of a statistical approach to these analyses was used to determine the distribution and phases of the components of brake pads.

SEM-EDS analysis of a ceramic brake pad

The overall EDS spectrum from the ceramic brake is shown in Figure 1. The chemistry (as determined by elemental composition) is included in Table 1 on the right side of the spectrum. Because large sections of the pad are composed of a carbon matrix – approximately 40% of the analyzed area is carbon – the carbon is omitted from the

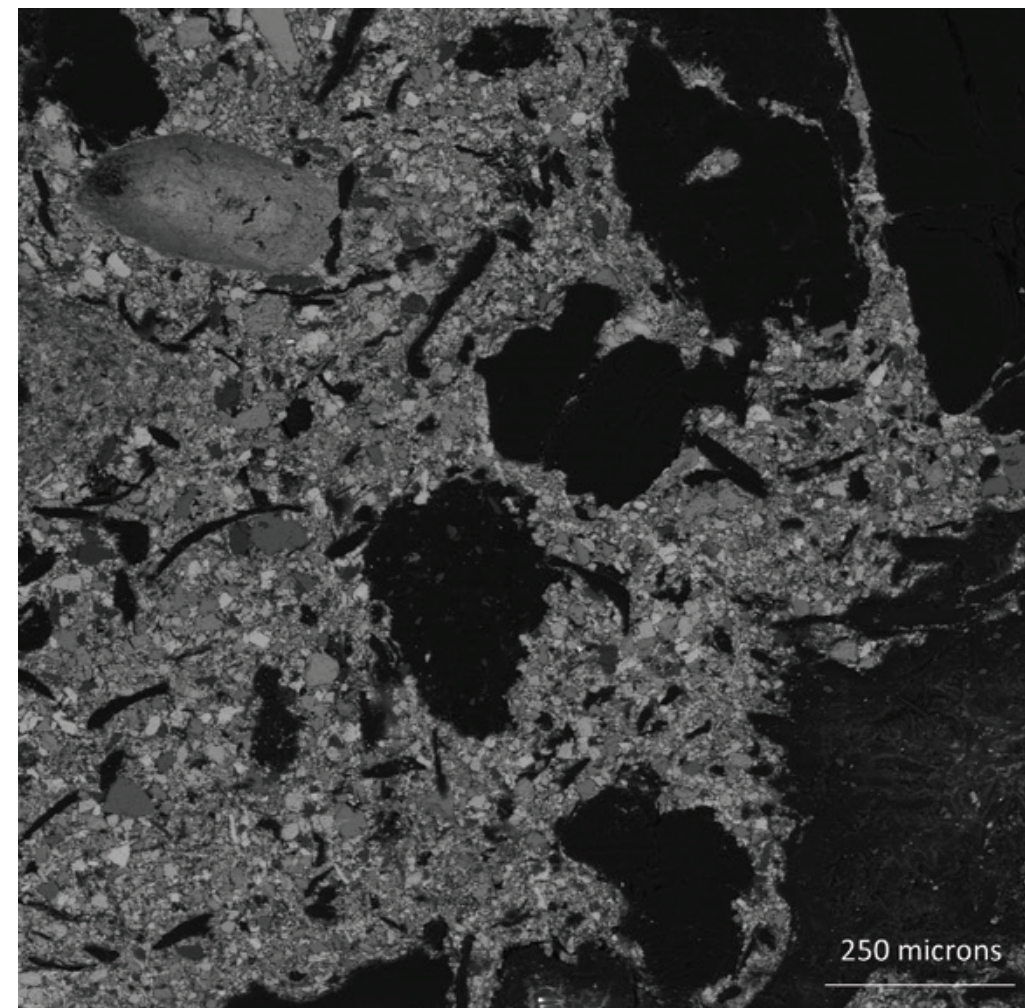


Figure 2. Backscatter electron image from the ceramic brake pad.

quantitative analysis in order to provide a clearer view of the chemistry in the non-matrix regions. The non-carbon matrix sections of the material are either metals, metal-oxides, sulfides or sulfates. The metal sulfides are attributed to the solid-lubricants, the Ba and Ca reflect the desire for stabilization against wear and high temperatures. The Fe along with the silicates provide the expected abrasive for friction-based braking.

The bulk spectral EDS analysis provides a general understanding of the elements present but is limited in information content. The backscatter electron image, Figure 2, reveals a strong spatial dependence on the elemental composition. Because brightness in an electron image is related to the atomic weight

of the elements in each region, the large, darker regions are expected to be the fibrous carbon matrix material. Within and around this matrix, the diverse regions of electron image contrast demonstrate a rich tapestry of elemental diversity with the expected metals, metal sulfides, silicates and other ceramic materials embedded within the carbon matrix.

While valuable, the chemical analysis of any electron image is entirely subjective. EDS, on the other hand, provides a detailed representation of the elemental distribution within a sample under study. The corresponding EDS x-ray element maps for the ceramic brake pad are shown in Figure 3. The individual element maps are shown in Figure

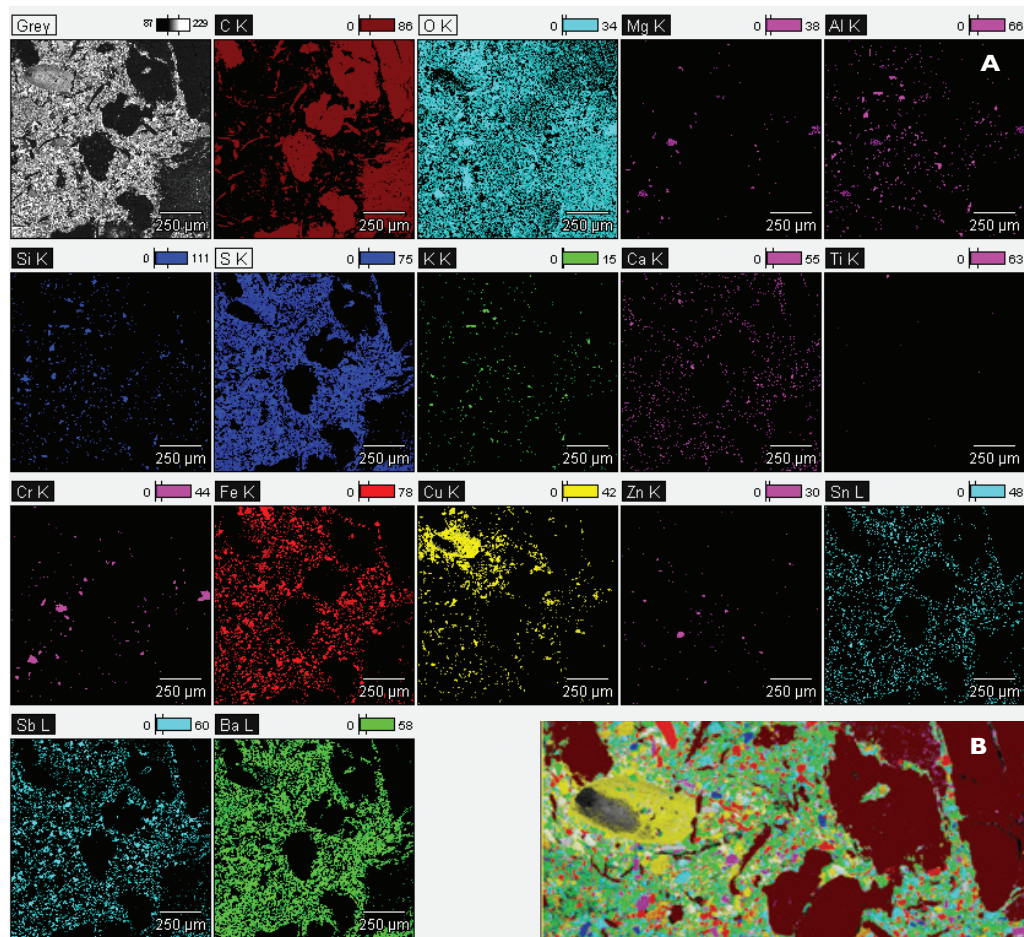
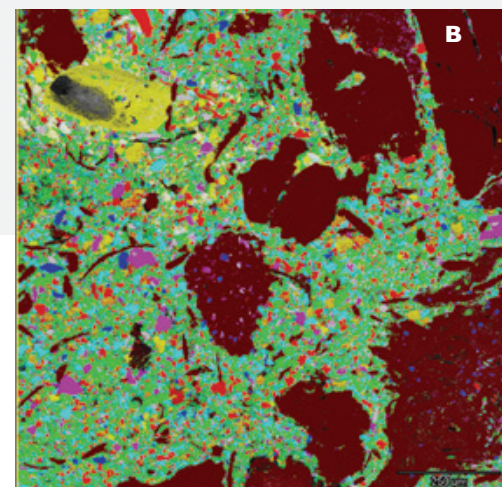


Figure 3. EDS x-ray element maps for the ceramic brake pad. (a) Individual element maps; (b) Element maps overlaid on the electron image. The colors from the element maps in (a) directly correspond to those in the overlaid image in (b).

3a. An overlay of the element maps on the electron image is shown in Figure 3b. From these element maps, the metallic, sulfide and silicate regions can be qualitatively identified. By overlaying selected elements together, the regions dominated by a collection of elements can be subjectively reviewed to identify trends and generalisations regarding the chemistry of the material under study. For example, it is interesting that while this pad is described as a “ceramic,” a very large portion (roughly 40%) of the elemental composition is formed from the carbon matrix. The implication is that this pad is more of a “semi-ceramic” than a “ceramic” formulation. Purely ceramic brake pads are prohibitively expensive in a consumer market. It is therefore



entirely understandable that most modern ceramic brake pads are composed of ceramic components within a carbon matrix material.

While the EDS element maps are effective at providing a certain level of qualitative information regarding the elemental composition of the brake pad, the analysis is subjective. There exists no mechanism to extract a purely unbiased and quantitative assessment regarding the chemical composition and distribution of each region within the brake pad material under study.

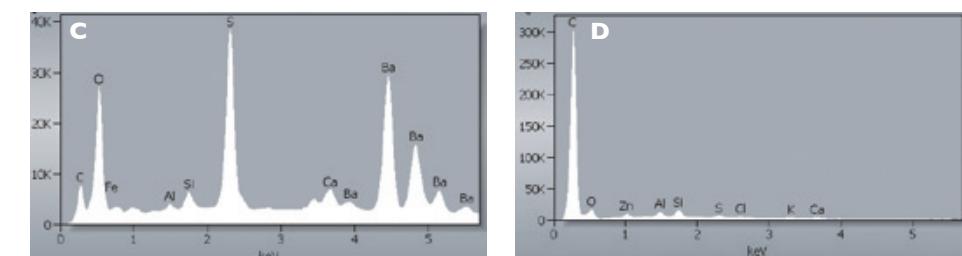
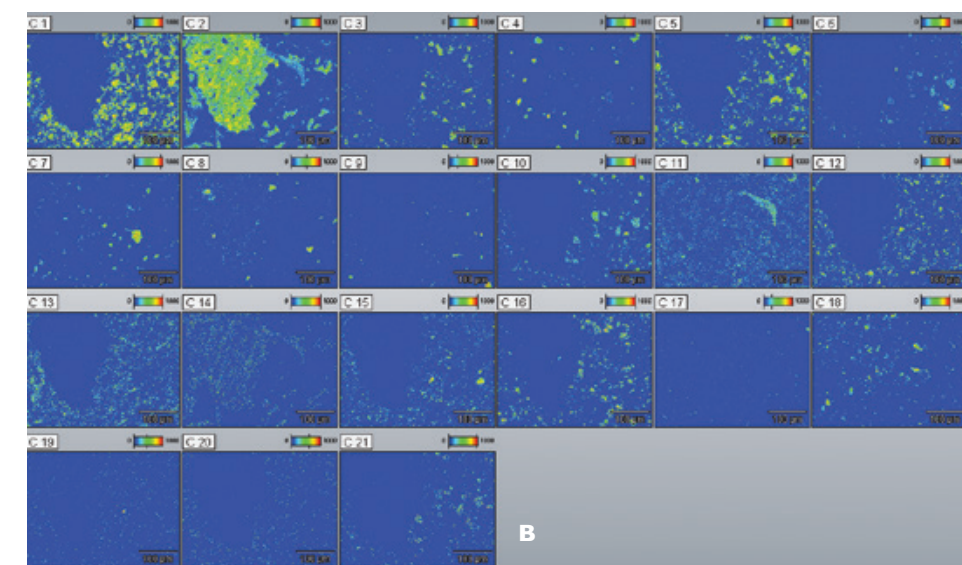
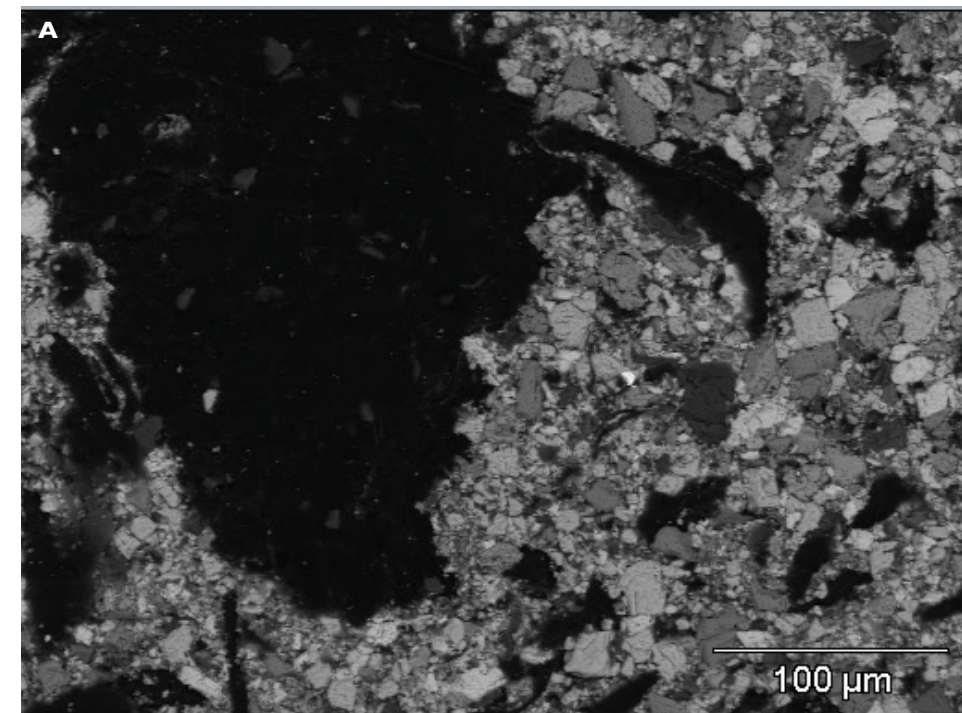


Figure 4. (a) Electron image from a section of the ceramic brake pad that was analysed; (b) Corresponding dominant component maps that were extracted from the same region using the COMPASS principal component analysis routine; (c) Spectrum associated with component 1; (d) Spectrum associated with component 2.

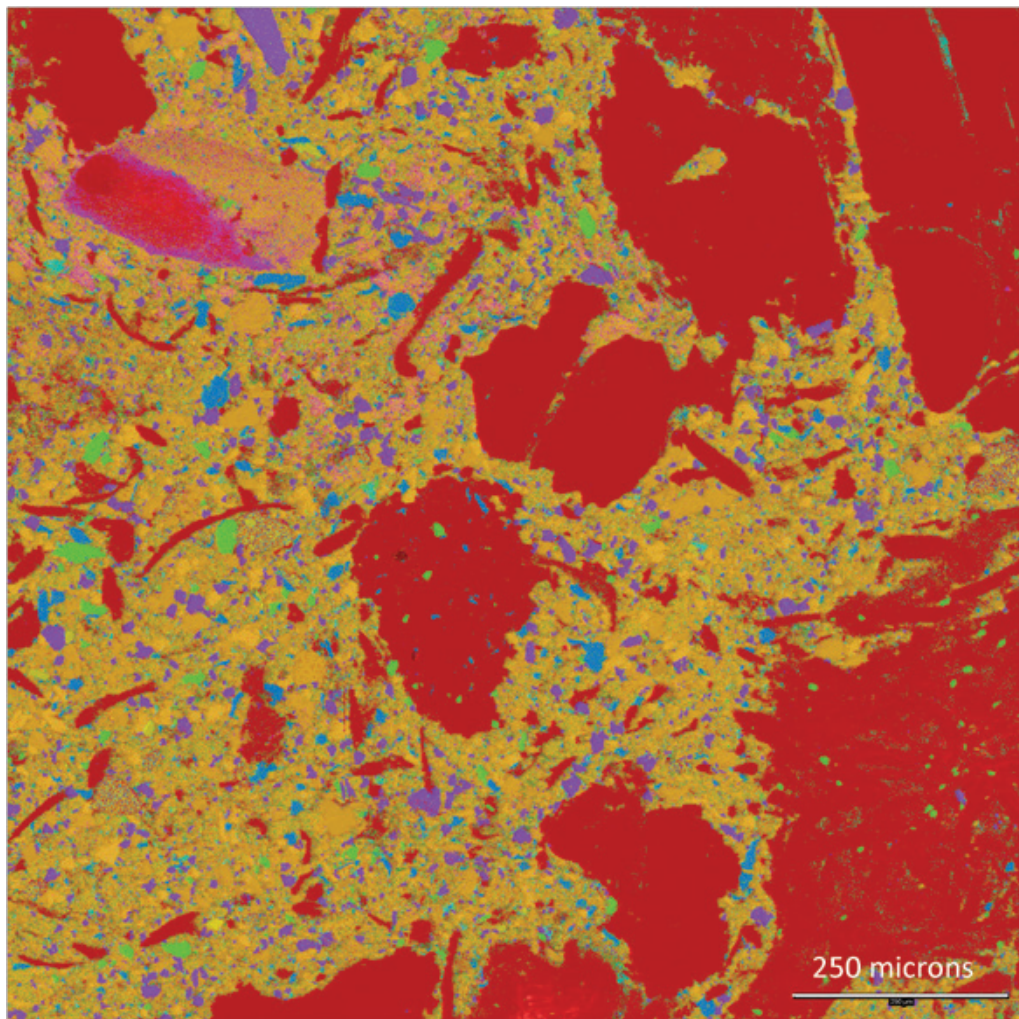


Figure 5. Quantitative EDS phase map of the ceramic brake pad. See Table 2 for associated colour key.

Quantitative Phase Mapping and Multivariate Statistical Analysis

Automated methods that employ sound statistical techniques are required to effectively analyse the large amounts of data involved in these EDS x-ray images in a consistent fashion that eliminates user bias. The key requirements for a robust system that automatically analyses these large EDS data sets are:

- (1) No assumptions about the absence or presence of any constituent element
- (2) The ability to handle noisy data
- (3) The ability to handle sparse and low volume data

- (4) The ability to handle significant spectral overlaps
- (5) Processing times of the same order or much less than the acquisition time for the data
- (6) Limited user inputs. The system developed in this present work meets all of the above requirements.

The routine described here for achieving Quantitative phase maps is based on the work performed and the patents granted to Paul Kotula and Michael Keenan at Sandia National labs. [5, 6] The commercialised routines, trade-marked as COMPASS, are further described in this white paper [7]. This routine is predicated on the

| Phase | Total | |
|---------------------------|-------|--|
| Carbon matrix | 40.42 | |
| Ba sulfate | 23.3 | |
| Ba sulfate with Sb and Sn | 11.49 | |
| Cu Fe sulfate | 7.03 | |
| Fe oxide | 6.84 | |
| Ca sulfate | 3.37 | |
| Fe Cu sulfide | 2.58 | |
| Al silicate | 1.71 | |
| Quartz | 1.12 | |
| Cr Mg Al oxide | 1.08 | |
| K Al silicate | 0.57 | |
| Zn sulfate | 0.47 | |
| Mg Fe sulfate | 0.03 | |

Table 2. Relative spatial coverage of each phase classified in the Quantitative EDS phase map of the ceramic brake pad in Figure 5 with the associated colour key.

understanding that while a complex system may be composed of millions of unique parameters, it can be nearly completely (> 99.9%) described by only a handful of dominant components. The routine, therefore, employs a form of principal component analysis in order to identify the minimum number of distinctive spectra and component maps that nearly completely describes the over-arching EDS data set.

An example of this approach is shown in Figure 4. Figure 4a shows the electron image from a section of the ceramic brake pad that was analysed. This section contains one million pixels. Each pixel, in turn, contains a complete EDS spectrum with 2000 discrete channels. The result is an EDS Spectral Imaging data set with two billion unique slices of data. Figure 4b shows the corresponding dominant component maps that were extracted from the same region using the COMPASS principal component analysis routine. Each of these thermal maps represents the probability that each pixel is statistically associated with that component map. Blue is 0%. Red is 100%. An EDS spectrum is associated with each component. As there are 21 component maps, there are then 21 associated spectra. As examples, the spectrum associated with component 1 and component 2 are shown in Figures

4c and 4d respectively. Examining the spectrum for component 1, Figure 4c, indicates that this is a region of barium sulfate. Examining the spectrum from component 2, Figure 4d, indicates that this is the carbon matrix. The value here is that the original map of one million pixels, each containing a unique EDS spectrum with 2000 channels, has now been distilled down to a readily understandable group of 21 distinct components that can each be examined and classified in turn.

In Figure 5, this approach is expanded from this single section to the entire collected area of study. For clarity, components that were correlated as statistically similar with a 90% confidence interval were combined together into a single component. This optional step enabled a further simplification to thirteen distinct components in the overall section studied. Each component was coloured and overlaid onto the electron image. Instead of showing each spectrum, the predominant elements within each spectrum were identified and the phases classified in Table 2. These elements are now used to describe the various components. In this way, the unique components have been used to transform all of the collected data into a Quantitative EDS “phase” map, where each phase represents a region of unique chemistry and where the chemistry is defined by the elements identified as present in each unique component. To this end, the surface area of each phase is also listed in Table 2.

The end result is a transformation from a detailed, very beautiful, EDS element map that provided only qualitative information as interpreted by the analyst to a fully quantified EDS phase map that requires no analyst interpretation in its creation and that can be used to make specific and informed decisions regarding the composition of this particular brake pad.

Studying the table of elemental phase and surface area now provides incredible insight into the target application of this brake pad. The largest region, colored red, is the carbon matrix which

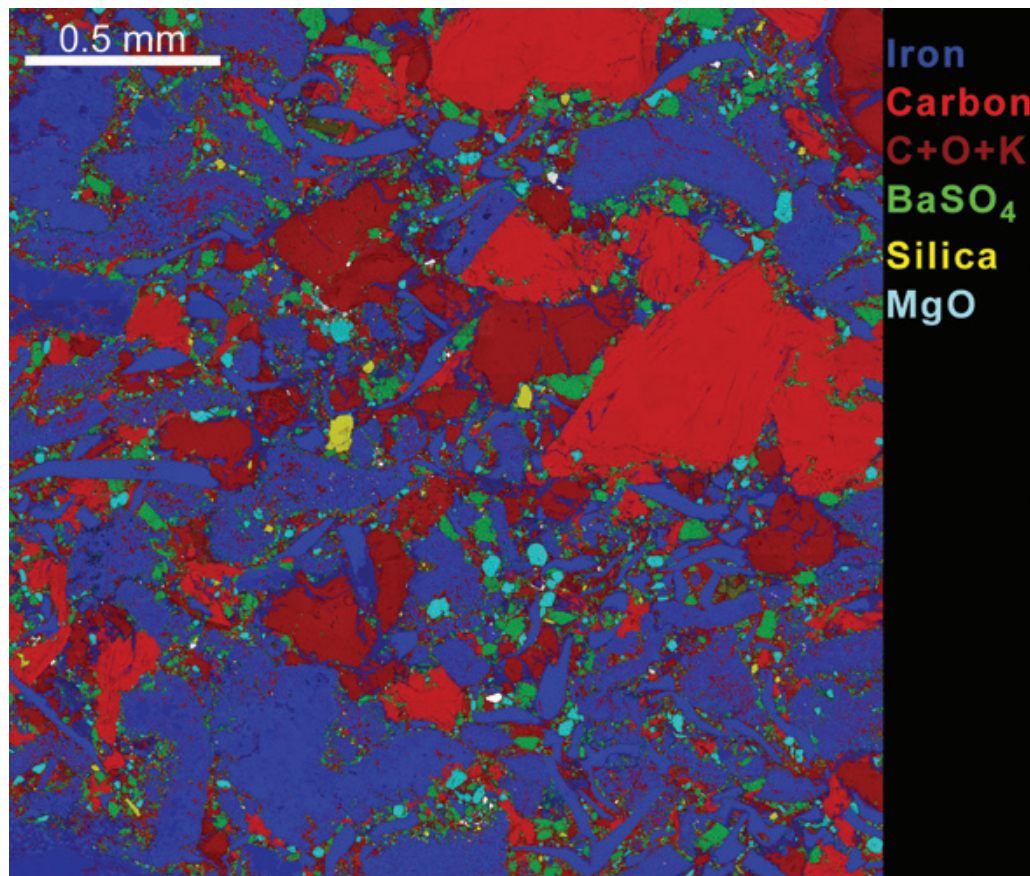


Figure 6. Quantitative EDS phase map of the semi-metallic brake pad.

constitutes roughly 40% of the material. The carbon matrix provides no real performance function during braking, but it does serve as a very low-cost means to form the overall structure of the pad. The second largest coverage is provided by the (orange) Barite (BaSO_4) rich regions. As discussed, the Barite serves as a stabiliser over a range of temperatures and environmental conditions and for wear resistance; i.e. longer life. Taken with the calcium sulfate regions, roughly one fourth of the area serves the purpose of stabilisation and wear resistance. This is followed by a wide variety of smaller metal sulfates and a fairly significant Ba–Sb, Sn–O region. These chemistries are associated with lubrication of the pad surface. This lubrication provides a smooth and quiet braking action. Finally, the metal oxides and silicates embedded within the larger regions compose the remainder of the material. These elements form the abrasives that

create the actual braking performance. It is worth noting that the friction surfaces of the pad only composes approximately 12% of the pad surface. The majority of the pad chemistry, therefore, is dedicated in this order: matrix, stabilisation and wear resistance, lubrication and finally friction or braking performance. This brake pad is clearly designed as a low-cost, sociable braking system, which is ideal for standard driving conditions in a city or suburb.

Analysis of a semi-metallic brake pad

This Quantitative phase mapping technique was next used to analyse a semi-metallic brake pad. The corresponding Compass phase map is shown in Figure 6. The field of view in this map is approximately 2.5 mm by 2.5 mm. The majority region in this pad, colored blue, is iron. The iron

covers nearly three quarters of the surface. The second most populous region is the carbon matrix (brown-red). This is followed by a relatively uniform distribution of smaller barite (green) and silica (yellow) regions. Both the iron and the silica provide the braking action. It is evident that the focus of the chemistry in this pad is prioritised as: braking performance, matrix, stabilisation and - to a smaller extent - lubrication, wear resistance and noise / dust reduction. This aligns well with the observation that semi-metallic brake pads are engineered – and advertised – for maximum braking performance at the cost of aggressive wear on the rotors and increased noise during braking. When compared to the ceramic pad studied, this particular semi-metallic brake pad is designed for much stronger braking action; possibly for improved safety for example during quick stopping of larger vehicles such as minivans or SUVs. There is less emphasis on noise and dust reduction. The predominance of iron points to a desire to keep costs low; although the wear on the rotors will increase overall maintenance costs as the rotors would be serviced more regularly.

Analytical summary

In the end, braking is a tradeoff. Ceramic pads are advertised as offering quieter stops, less dust and longer pad life. The downside is a lower coefficient of friction and less effective overall braking performance relative to semi-metallic pads. Semi-metallic pads, on the other hand, are described as producing more noise and dust but provide a stronger, more consistent braking performance.

The unique chemistry of the braking surface of the pad on the micro-scale drives the macro-level performance. While SEM-EDS offers a qualitative review of this micro-scale chemistry, it lacks the rigorous quantitative detail that can drive confident decisions during composite engineering – for example when comparing macro-level performance characteristics to the underlying chemistry – or during quality control – for example when

comparing test sections from many hundreds of pads in high volume production.

Utilising a principal component analysis technique as described here, the dominant components can be extracted and converted into a modest number of phases that can be classified by chemistry and area coverage in order to provide a consistent and reproducible method of comparing the chemical composition in one pad against that of any number of other brake pads. This data can then be readily monitored and reviewed; for example, plotted and monitored using statistical process control techniques. In this case, the COMPASS principal component analysis routine was able to quickly differentiate the underlying chemistries of a ceramic brake pad and a semi-metallic brake pad and to relate those differences to the advertised differences in overall braking performance.

References

1. Uexkull, S. Skerfving, R. Doyle, M. Braungart (2005). Antimony in brake pads-a carcinogenic component? *Journal of Cleaner Production*. Vol. 13 pp. 19-31.
2. Blau (2001). *Compositions, Functions, and Testing of Friction Brake Materials and Their Additives*. ORNL/TM-2001/64 Pub57043.
3. Amato, O. Font, N. Moreno, A. Alastuey, X. Querol (2012). Mineralogy and Elemental Composition of Brake Pads of Common use in Spain. *Revista de la sociedad espanola de mineralogia*, pp. 154-155.
4. G. R. Kumar, S. Thriveni, M. R. Reddy, G. H., Gowd (2014). Design Analysis & Optimization of an Automotive Disc Brake. *International Journal of Advanced Engineering Research and Science (IJAERS)*. Vol-1 Issue-3, p. 24-29.
5. P. G. Kotula, M. R. Keenan, J. R. Michael (2006) *Microscopy and Microanalysis* 12 (2006) pp. 36-38, 538-544.
6. West (2015) *Principal Component Analysis in EDS: The COMPASS Algorithm*, Thermo Fisher Scientific white paper WP52773.