

Soot and Ash Deposition Characteristics at the Catalyst-Substrate Interface and Intra-Layer Interactions in Aged Diesel Particulate Filters Illustrated using Focused Ion Beam (FIB) Milling

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ABSTRACT

The accumulation of soot and lubrication-derived ash particles in a diesel particulate filter (DPF) increases exhaust flow restriction and negatively impacts engine efficiency. Previous studies have described the macroscopic phenomenon and general effects of soot and ash accumulation on filter pressure drop. In order to enhance the fundamental understanding, this study utilized a novel apparatus, that of a dual beam scanning electron microscope (SEM) and focused ion beam (FIB), to investigate microscopic details of soot and ash accumulation in the DPF. Specifically, FIB provides a minimally invasive technique to analyze the interactions between the soot, ash, catalyst/washcoat, and DPF substrate with a high degree of measurement resolution.

The FIB utilizes a gallium liquid metal ion source which produces Ga^+ ions of sufficient momentum to directionally mill away material from the soot, ash, and substrate layers on a nm- μm scale. As the FIB cuts into the sample, uncovering intra-layer details, the coupled high resolution SEM imaging and energy dispersive x-ray (EDX) analysis provide both morphological and chemical data. This tool was applied to investigate soot and ash accumulation in the DPF, with a specific focus on characterizing interactions between the soot/ash/DPF interfaces, such as soot penetration into the ash layer, as well as soot and ash accumulation in the DPF surface pores. In particular, ash and soot particle size, layer pore structure, and the extent of penetration or intra-layer mixing, are all parameters directly impacting DPF pressure drop, which may be quantified using this technique. The work in this study leveraged existing databases of aged DPFs containing various levels of soot and ash, originating from field trials and controlled laboratory testing. Results obtained with this technique provide a fresh and complementary perspective, as well as additional details useful to understand the macroscopic observations of the combined ash and soot effects on diesel particulate filter pressure drop.

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INTRODUCTION

The impact of ash accumulation on the overall performance of the engine and aftertreatment system is dependent on a number of parameters, including the amount of accumulated ash, its distribution in the DPF, and the specific properties of the ash deposits. To further complicate matters, many of the parameters, described above, are also influenced by a host of other factors including lubricant additive chemistry, exhaust conditions, engine operation, and the specifics of the filter material itself. Accurate characterization of ash morphology, measurement of ash properties, and observations of the manner in which ash interacts with the DPF are key to understanding the

fundamental mechanisms responsible for determining how ash impacts DPF performance.

Generally diesel particulate filters consist of a honeycomb monolith, primarily cordierite or silicon carbide, with porous channel walls, alternately blocked at each end. As the particulate matter (PM) -laden exhaust gases enter the open channels at the inlet of the filter, the gases are forced to flow through the porous channel walls and out the exit channel. In the process, the PM is trapped either in the porous walls or in a cake layer along the surface of the filter [1]. Following PM accumulation, it may be either periodically or continuously removed from the filter via oxidation (regeneration), leaving a small amount of incombustible ash behind. Generally the

ash comprises less than 1% of the PM, and may accumulate in the filter over time [2]. The ash deposits may exist in a layer along the channel walls or in end-plugs at the back of the filter channels [3,4], with the distribution of the ash affected, to some extent, by the operating history of the DPF [5, 6, 7, 8].

In addition to performing a filtering function, many commercial diesel particulate filters also employ some form of catalytic coating to promote soot oxidation (regeneration) at lower temperatures. Typically the catalyst is deposited on the filter surface along with a washcoat, which helps to bind the catalytic particles to the filter walls. Some of the most prevalent catalyst components include platinum, Pt, palladium, Pd, and Rhodium, Rh, although a number of other components may also be used. Additional elements commonly found in the washcoat include cerium, Ce, and aluminum, Al, among others.

Thus the diesel particulate filter itself is a relatively complex system consisting of multiple components, performing several very different functions. It is also important to note the wide range of length scales necessary to accurately describe DPF operation, which varies from tens of centimeters to describe the overall filter geometry to tens of microns for DPF pore sizes, to single digit nanometers for individual catalyst particles. Given the size of the particles trapped in the DPF, ranging from 10-100 nm for soot particles, to 1-10 μm for typical ash primary particles and agglomerates [6], understanding the interactions of the trapped particles with the DPF at these length scales is critical to explaining the macroscopic behavior and performance of the particulate filter.

Analysis of typical DPF ash deposits generally shows the majority of the ash originating in the lubricant additives, with the most prevalent ash components being Ca, Mg, and Zn in the form of various sulfates, phosphates, and oxides [4,9, 10, 11]. Previous work has shown a difference in pressure drop across the DPF by up to a factor of two, for the same mass of ash, but with variations in ash composition [4], thus emphasizing the need to fundamentally understand the factors controlling ash properties in the DPF. While much work has been done to describe the macroscopic effects of ash accumulation on DPF performance in terms of flow restriction, pressure drop, and to a lesser extent catalyst interactions, much information related to the fundamental ash properties and their interactions with the various DPF components remains unknown.

ASH ANALYSIS

Although quantitative measurements of ash properties such as mean particle size, packing density, porosity, and mean pore size are key to explaining the observed ash effects on DPF performance, obtaining this information can be quite challenging using conventional techniques. A survey of the literature in 2009 showed differences in ash properties reported by up to two orders of magnitude between studies

[6]. While measurement of certain ash properties, such as ash layer thickness and packing density for example, may be fairly straightforward, determining ash particle size or porosity is much more complex, and oftentimes requires the development of new and more advanced analytical techniques.

Of additional concern when characterizing ash samples, is not only the application of the measurement technique, but the sample preparation process. Conventional approaches to applying scanning electron microscopy (SEM) and similar optical analysis to DPF and ash samples generally require the sample be disturbed in some fashion to expose the region of interest. Common means of sample preparation include physically cutting the DPF into smaller sections, or even breaking open individual channels to allow for direct optical access [4]. Furthermore, a large portion of the observed ash effects on DPF performance (whether related to flow restriction of catalyst interactions), is believed to occur at the interface of the particular components present in the system, such as between the ash particles and DPF pores, or ash layer and catalyst particles, for instance. Detailed analysis on the small length scales required to describe the interactions between the soot, ash, catalyst/washcoat, and DPF layers, can easily be complicated by artifacts introduced via sample preparation.

In order to overcome some of these challenges, several innovative techniques have been applied to understand the manner in which the trapped particles inside the DPF interact with the filter on the micro-scale. Most notably, a series of studies conducted by the Tokyo Institute of Technology beginning in 2003 used small DPF core samples, with optical access enabled via a quartz window installed over several DPF cells. Coupled with an optical microscope, this system enabled in situ observations of PM accumulation and regeneration in the DPF, both in the cake layer, as well as quantification of particle penetration into the DPF pores [12, 13, 14].

More specific to ash accumulation in the DPF, recent work by Hitachi reported ash particle size measurements conducted using SEM. The authors observed larger particles formed following high temperature regeneration events (due to increased agglomeration) and smaller particles formed at lower temperatures [5]. Additional studies further report on the regular application of SEM either alone or in conjunction with energy dispersive x-ray analysis, to characterize ash morphology and elemental distribution in the DPF and various other aftertreatment system components [4,15,16]. While extremely useful in the detailed information obtained through the application of these techniques, questions related to the influence of sample preparation still remain.

Non-destructive tools such as X-ray computed tomography (CT) [17] and neutron computed tomography (nCT) [18] provide three dimensional data to describe soot and ash distribution over the entire filter. While these methods do not disturb the sample, both tools are somewhat

limited for applications requiring small measurements of sample details at length scales less than 50 μm .

This study addresses several of the issues outlined above, through the application of advanced diagnostics using a minimally invasive approach to better characterize the specific interactions between the accumulated ash particles and DPF system components. Specifically, this work describes the application of focused ion beams (FIB) to essentially mill through the soot, ash, catalyst, or washcoat layers on a micron scale to expose sub-surface details such as the underlying interfaces and particle interactions. Coupled with high resolution SEM imaging and EDX elemental analysis, this technique provides a promising new tool to provide much of the fundamental information required to explain the mechanisms by which these microscopic ash particles affect DPF performance on the macro-scale.

FIB INTRODUCTION

Focused ion beam milling, as the name implies, utilizes a concentrated beam of energetic ions to remove material from a sample surface. The ion beam apparatus is inherently similar to a scanning electron microscope, however energetic ions, instead of electrons, are fired through electrostatic lenses, instead of electromagnetic lenses, to a fine point on the sample surface. Ions are more massive than electrons and have significantly higher momentum when colliding with a sample surface, which, depending on the relative magnitude of the momentum, will result in either or both destructive and non-destructive interactions. Focused ion beam milling can be utilized over a very large range, from around 5-10 nm to 100-200 μm , and has been an important experimental and fabrication-related tool for numerous research areas and industries for the last 20 years [19].

The energetic incident ion will interact in different ways with a sample, depending on the accelerating voltage applied by the focused ion beam apparatus. Two of the main uses of focused ion beams, which utilize two very different ion-sample interactions, are ion implantation and focused ion beam milling, the focus of this article being the latter. Focused ion beam implantation is essentially a material property alteration where semiconductor dopant species such as As, P, B, BF₃, In, Sb, Ge, Si, N, H and He are inserted into the atomic structure of silicon integrated circuits [20, 21, 22, 24]. Focused ion beam milling, on the other hand, is a destructive, momentum transfer-driven technique where ion-sample interactions will displace atoms from the sample structure by ejecting them from the sample surface in a phenomenon otherwise known as sputtering. The sputtering of sample atoms can be carefully controlled by adjusting the ion beam accelerating voltage and current in order to function as a mechanical milling machine on the nano- and micro-scales, therefore providing the possibility to expose otherwise hidden sample features.

FIB APPARATUS

Most commercial focused ion beam systems utilize liquid metal ion sources (LMIS) to generate ions, where current ion sources include Al, As, Au, B, Be, Bi, Cs, Cu, Ga, Ge, Er, Fe, H, In, Li, Ni, P, Pb, Pd, Pr, Pt, Si, Sn, U and Zn [22]. The ion source takes advantage of materials with low melting temperatures, volatilities and vapor pressures, such as Ga, which has been used as the ion source in this study. The ion source is placed at the end of a sharp needle, usually W, and a strong electric field (approximately 10^{10} V/m) is applied between the tip of the needle and the extraction aperture through which the ions are accelerated [25]. The ions travel through one or two lenses, depending on the apparatus. This study utilized a two lens system, including both electrostatic condenser and objective lenses and a beam blaster. The beam column was kept under approximately 10^{-7} mbar, the accelerated voltage ranged from 10-50 keV or higher with a relatively narrow energy distribution, and the beam current ranged from 1 pA to 20 nA resulting in a range of 2-12 A/cm² for the current density [19,24,26].

FIB PRINCIPLES

The interaction of the incoming ion with the sample can generally be classified as either elastic, involving nuclear energy loss, or inelastic, involving ions losing energy to sample electrons [25]. Such interactions result in the sputtering of sample atoms, emission of ions, electrons and radiation. The particles emitted during ion bombardment can give additional information about the sample, in particular ion induced secondary electron imaging (ISE) which gives increased contrast to metal grain boundaries, and secondary ion mass spectroscopy (SIMS) [19,25]. Figure 1 depicts the process of an incident ion interacting with the sample whereas the aforementioned interactions are graphically explained.

Essentially, when an ion with a given energy comes in contact with the sample surface, the ion collides with the sample atoms and electrons with a large enough momentum to displace the sample atoms from their lattice positions. The incoming ion is accelerated to ≥ 20 keV, whereas typical surface binding energies for sample atoms are 1-5 keV. Therefore, the energetic ion continues to displace sample atoms until its energy has been reduced below a critical value in which case the ion will become implanted in the sample structure. The ion-atom collisions are well understood, by means of the collision cascade model which assumes independent binary collisions, and can be calculated to obtain an approximate understanding of the extent of sputtering and ion implantation that occurs during focused ion beam milling [25]. The penetration/implantation depth and scatter of the ions is of interest for control aspects of the focused ion beam milling technique and is calculated using the Transport of Ions in Matter (TRIM) software, which uses a Monte Carlo simulation of ion-atom collisions from a quantum mechanics

perspective [27]. A sample TRIM simulation relevant to the samples in this study is given in the following figure.

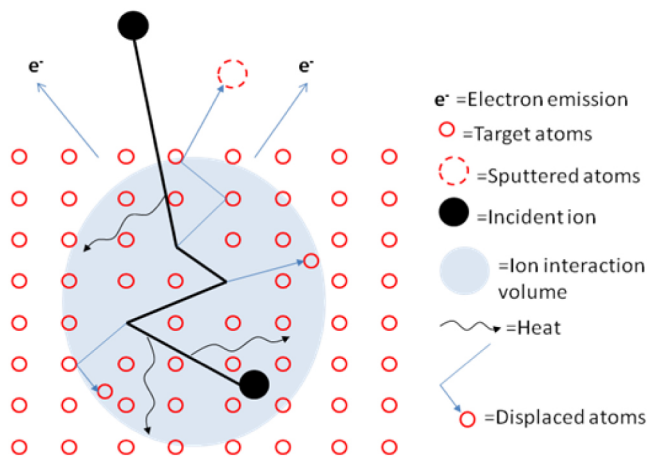


Figure 1. Graphical representation of the ion-atom interaction in the sample where the ion path in the sample is not a straight line due to deflection from sample atoms and where heat and secondary particles are emitted.

This simulation shown in [figure 2](#) uses 1000 Ga ions, initially at 30 keV, and a carbon sample or target which is plotted from the sample surface, on the left side of all images above, to 500 Å into the sample. The simulation can be summarized by stating that the mean penetration depth was found to be 233 Å and the mean lateral spread was found to be 34 Å, both of which are inversely proportional to the sample density in general. In addition, the sample sputtering yield was calculated to be 1.82 C atoms/ion. Although soot is a porous agglomeration of semi-spherical particles, the aforementioned simulation is relevant because the average soot particle size is much larger than the calculated ion range and spread. A rule-of-thumb for estimating the mean projected ion range into a sample is that the incident ion energy in keV is approximately the average ion penetration depth in nm in the sample [28], which agrees roughly with the above TRIM calculations where a 30 keV Ga ion beam shows average penetration depth of roughly 30 nm (TRIM gave 23.3 nm).

The specific ion interaction of interest in this study is that of sample atom sputtering, which is a function of the sample material, sample temperature, crystal orientation, angle of incidence, ion mass, ion beam scanning speed, ion energy and the amount of sample material re-deposition [22,25,29,30]. Therefore, the milling process is a delicate balance between sample-specific and FIB-specific properties. In the case of this study where the inhomogeneous samples include a wide range of densities, thermal conductivities, and related parameters, milling becomes quite complex. In general, ion energies of 10-100 keV are used for sputtering, where the sputtering yield ranges 1-50 atoms/ion, however significantly higher sputtering yields can be achieved by using localized

reactive gas injections such as Cl_2 [22,24]. Therefore, by carefully controlling the ion beam accelerating voltage, current, incident angle and scanning speed, among other variables, a sample can be milled with a very high degree of precision, as demonstrated in this study.

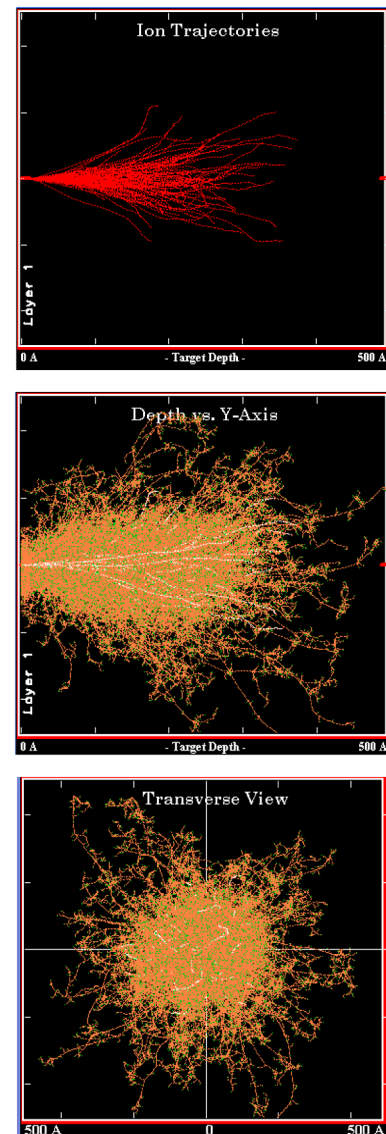


Figure 2. TRIM simulations for ion trajectories (top), ion penetration depth with recoiled carbon atoms (middle) and lateral ion spread with recoiled carbon atoms (bottom).

FIB DRAWBACKS

As previously mentioned ion-atom interactions in the sample result in a number effects, some of which are undesired. Sample surface swelling due to amorphization has been observed to occur when the ion concentration is too low, for example milling with an ion concentration of approximately 10^{15} Ga ions/cm² showed maximum swelling whereas higher ion concentrations, on the order of 10^{17} Ga

ions/cm² reduced the effect [31]. Effects such as phase formation, grain transition, point defect creation and structural dislocation have also been observed and studied [25]. Ion beam induced heating can occur locally in the sample, and example calculations are given in the [appendix](#). In addition, the FIB milling technique is utilized on very small sample areas and therefore requires that multiple sites on the same sample are investigated with this technique for representative data.

EXPERIMENTAL SET-UP AND PROCEDURES

FIB analysis was applied to existing ash-loaded DPF samples originating from particulate filters either loaded with ash in the laboratory or installed on vehicles operating in the field. While the complete DPF operating history and lubricant formulations are well-known for the DPF samples loaded with ash in the laboratory, much less information was available for the field ash samples.

SAMPLE HISTORY

All of the DPF samples previously loaded with ash in the laboratory were subjected to an accelerated ash loading procedure developed at MIT. Ash accumulation in the laboratory, under specific, controlled conditions, ensures the filter operating history is well-known and enables correlations between exhaust conditions, lubricant chemistry, and ash properties to be determined. On the other hand, while DPFs from field applications provide the most realistic specimens for analysis, data analysis and interpretation is difficult due to lack of information related to the filter's operating history and conditions.

The laboratory ash loading process has been described in detail previously [6,32,33]. The accelerated ash loading and aftertreatment aging system was designed to load a conventional D5.66 "(14.38 cm) X 6" (15.24 cm) DPF to 40 g/l of ash in slightly under 100 hours. This system is used in conjunction with a Cummins ISB 300 engine to enable the feed-gas particulate and ash characteristics to be carefully controlled and monitored. In its most basic form, the accelerated ash loading system produces soot with high ash content via the integration of a secondary diesel burner and oil injection system into the exhaust of the Cummins ISB. This system further allows for control and acceleration of specific oil consumption mechanisms, enabling the simulation of engine-out ash and PM as closely as possible. Previous studies showed similar exhaust ash emissions characteristics between the accelerated ash loading system and Cummins engine [32]. More recently, a comparison of DPFs aged in the laboratory using the accelerated ash loading system with filters subjected to 180,000 miles of on-road fleet testing using CJ-4 oils showed ash properties, distribution, and composition to be quite similar for both the laboratory and field-aged filters [6].

Several different lubricant formulations were used with the laboratory ash-loaded filters. The predominant lubricant, a commercial CJ-4 oil, served to define the baseline. Three other lubricants, each consisting of the same base oil, but containing only one additive component were also employed to control the composition of the ash in the DPF. All of the oils were formulated to the 1.0% sulfated ash level. Calcium-based detergent, magnesium-based detergent, and zinc-based anti-wear/anti-oxidant additives were selected for the individual lubricant formulations, as these are among the most prevalent elements found in DPF ash [4,9,10,11].

All of the cordierite diesel particulate filters loaded with ash in the laboratory measured D5.66 "(14.38 cm) X 6" (15.24 cm) giving a total DPF volume of 2.47 liters with a cell geometry of 200 cells/in.² (31 cells/cm²) and wall thickness of 0.012 in. (0.30 mm). All of the filters were coated with a platinum catalyst and washcoat. The filters were loaded with ash using the accelerated ash loading system to simulate either active (periodic) or continuous (passive) regeneration.

The maximum specific DPF ash load achieved for the laboratory-aged DPFs was 42 g/l. This level of ash accumulation is estimated to be equivalent to roughly 240,000 miles (386,000 km) or 5,960 hours of DPF operation. This estimate is based on the following assumptions for a typical medium heavy-duty diesel engine: 15 g/hr average oil consumption [34], 40 mi/hr (64 km/hr) average speed, and a full sized particulate filter volume of 12 liters. In some cases different levels of ash loading were desired, with correspondingly different on-road equivalent distance/hours.

In addition to the DPFs loaded with ash in the laboratory, several cordierite field-aged DPFs from fleet test vehicles were investigated. All of the field-aged filters were operated with engines using commercial CJ-4 oils for at least 150,000 miles, on an OEM application (no retrofit filters). While the operating history, lubricant formulations, and ash properties of the DPF samples loaded with ash in the laboratory are well-known, much less information was available for the field-aged filter samples.

FIB SYSTEM

A Helios Nanolab 600 Dual Beam focused ion beam milling system from FEI was used in this study. The Nanolab 600 provides an ion beam with up to 20 nA current and 0.5-30 kV acceleration voltage with a liquid gallium ion source, which is capable of ion imaging resolution of 5nm at 30 kV. The SEM in this instrument includes a magnetic immersion mode which is capable of 0.9 nm resolution at 15 kV and an acceleration voltage range of 0.35-30 kV. Some of the measurements included in this article utilize image processing software, ImageJ, which allows quantification of images obtained from the Helios SEM.