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ABSTRACT

Compositions in the mixed strontium/calcium feldspar ($[\text{Sr}/\text{Ca}]\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) - aluminum titanate ($\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$) system have been investigated as alternative materials for the diesel particulate filter (DPF) application. A key attribute of these compositions is their low coefficient of thermal expansion (CTE). Samples have been prepared with porosities of >50% having average pore sizes of between 12 and 16 μm . The superior thermal shock resistance, increased resistance to ash attack, and high volumetric heat capacity of these materials, coupled with monolithic fabrication, provide certain advantages over currently available silicon carbide products. In addition, based on testing done so far aluminum titanate-based filters have demonstrated chemical durability and comparable pressure drop (both bare and catalyzed) to current, commercially available, silicon carbide products.

INTRODUCTION

Diesel particulate matter (PM) emissions pose serious health concerns and are under environmental regulation. Diesel filter after-treatment technology is currently used to remediate PM emissions. SiC and cordierite filters are two of the most viable solutions available for use today. Cordierite has a low coefficient of thermal expansion and can survive thermal shock in this application, but cordierite is limited by its low heat capacity. It is also susceptible to ash reaction during exceedingly high temperature applications [1]. SiC, on the other hand, has a lower thermal shock resistance and thus needs to be segmented. The segmentation increases manufacturing costs and is a concern because of potential mechanical integrity issues. Other issues with SiC have been reported recently and solutions have been implemented [2-3].

An alternate DPF candidate is a novel Aluminum Titanate (AT) ceramic oxide composite. The composition is highly refractory with a melting temperature exceeding 1500°C. The high heat capacity of the composition is an attribute that is beneficial for thermal management and allows the filter regeneration temperature to be low. Although the intrinsic coefficient of thermal expansion of aluminum titanate is quite high ($\text{CTE} = >9 \cdot 10^{-6}/^\circ\text{C}$), the

composite AT composition discussed herein has excellent thermal shock resistance due to the lower thermal expansion of the secondary phases and microcracking of the AT phase. Microcracking is a feature that has been used successfully for cordierite in catalytic converters. In addition, Sakai and Bradt have demonstrated that microcracking can be used to improve the toughness and increase the thermal shock resistance of a ceramic [4].

In this study, an overview of the compositions, processing, and resulting material properties of this novel AT composition are presented. Two generations of compositions are discussed showing subsequent improvement of the porosities. Strategies for optimization of the porosity are presented resulting in considerably lower backpressures. Finally, the durability is investigated under various conditions. The material has met internal durability requirements for the DPF application.

COMPOSITION

The strength of pure aluminum titanate ceramics is limited due to extensive microcracking [5], which results from the crystallographic thermal expansion anisotropy. In order to simultaneously optimize CTE, strength, and durability, an additional phase or phases are required. The first generation AT composition (AT-Gen A) was based on the pseudo phase diagram shown in Figure 1.

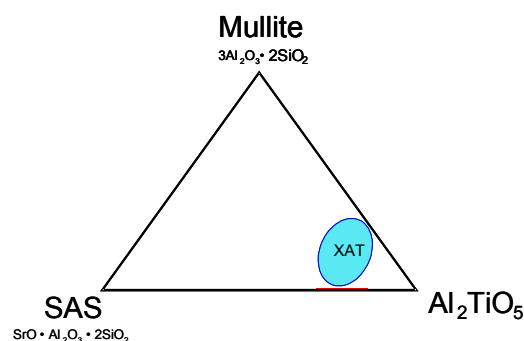


Figure 1. AT-Gen A Phase assembly diagram

The composition was batched to include 7.5% mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), 22.5% strontium feldspar ($\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and 70% aluminum titanate [6]. Less than 0.25% iron oxide (Fe_2O_3) was added to the batch. The Fe_2O_3 forms a solid solution with the aluminum titanate phase, and improves the thermal decomposition resistance of the AT phase [7]. The processing and other components, including the resulting properties will be discussed in the next two sections. Subsequent generations of the AT composition aimed at increasing porosity, reducing CTE, and improving strength and durability resulted in the current composition (AT-Gen B) which incorporates pore formers and includes calcium. The calcium is added to form a solid solution of a mixed Feldspar ($\text{CaO}, \text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) [8]. Approximately 4% of the current batch is Ca-Feldspar ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), leaving a reduced strontium feldspar level of 18.5%, and the same levels of mullite and aluminum titanate as described previously. In addition, the AT-Gen B composition has no Fe_2O_3 additive.

MATERIALS AND PROCESSING

The ease of processing and the choice of standard raw materials associated with this oxide composite make it attractive. A desirable feature of aluminum titanate filters is that the firing temperatures can be as low as 1400°C , and is done in air [9]. Another desirable processing advantage of the AT DPF is that it is extruded as a monolith. According to the current information available to us this does not seem to be the case with SiC filters which require assembly of extruded SiC segments and higher firing temperatures under controlled atmosphere. In addition, segmentation of SiC might pose potential mechanical integrity issues and decreases open frontal area.

For extrusion of the AT oxide composite, fine powders of the raw materials are batched together, mullied and extruded as illustrated in Figure 2 below. The resulting monolith after extrusion is dried and fired, and finally plugged to make a DPF.

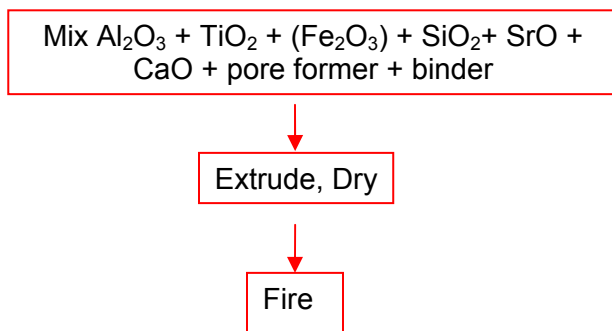


Figure 2. Processing Steps for AT Filters

METHOD FOR POROSITY IMPROVEMENT

For the first generation of AT, no calcium or pore former were added to the composition. The porosity was

achieved simply by reactive sintering of known precursor materials, with the pores being formed during the evolution of the reaction. The particle size of the starting materials were optimized to improve the resulting porosity; typically 40-42% for the first generation. An example of the resulting microstructure showing the highly microcracked nature of the material is shown in Figure 3. The microcracks come from the anisotropy in CTE of the aluminum titanate and the mismatch of the CTE of the individual phases, resulting in a composite with an overall low CTE and elastic modulus. The result is a highly thermal shock resistant material.

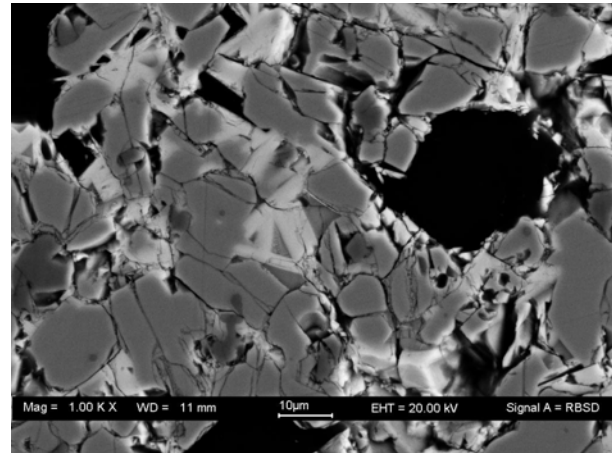


Figure 3. SEM Image of the Polished Cross Section of AT-Gen A.

The white phase in the upper SEM is the Sr-feldspar phase, while the gray phase is the aluminum titanate phase which is mixed with some glass, trace alumina and titania.

The next generation of AT incorporated changes in the particle sizes of the starting raw materials and the addition of pore formers to increase the porosity to 51% and create a well connected microstructure. In addition, Fe_2O_3 was removed from the batch after durability studies indicated that compositions without it passed internal durability requirements. Finally, calcium was added in order to improve property uniformity and ease processing.

ALUMINUM TITANATE DPF PROPERTIES

Table 1 lists the properties of the two generations of AT discussed herein.

Table 1. Physical Properties of AT Compositions

	AT-Gen A	AT-Gen B
% porosity	41	51
Pore Size (μm)	17	15
CTE ($\times 10^{-7}/^\circ\text{C}$; 1000°C)	5	9
MOR (PSI [MPa])	206 [1.42]	213 [1.47]
eMod (PSI $\times 10^5$ [GPa])	2.65 [1.83]	2.10 [1.45]
Firing Temperature ($^\circ\text{C}$)	1500	1450

The progression of properties from a product with 41% porosity to one having 51% porosity is clearly evident in the SEM images in Figure 4. The polished cross sections clearly show more porosity with a more evenly distributed pore size in the Gen B composition. By achieving such a distribution without the large pores observed in the Gen A composition, we have been able to maintain nearly the same strength with 10% higher porosity.

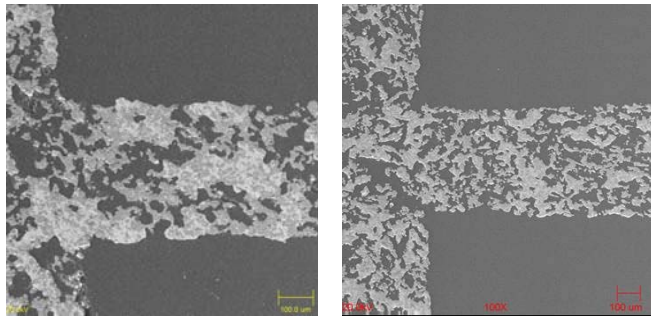


Figure 4. Polished Cross Section SEM Images of AT-Gen A (left) and AT-Gen B (right), both at 100X.

The properties of the latest version of AT are compared with those of a commercially available SiC product in Table 2. The most striking difference is, of course, the CTE which requires the SiC product to be fabricated in segments. The mechanical strength of SiC is over 5 times higher than it is in AT. On the other hand the thermal shock parameter (TSP), which is a calculated value based on mechanical strength, CTE and e-modulus values [10], is nearly an order of magnitude higher for AT, indicating this material's greater resistance to thermal shock and ability to fabricate it as a monolith. In addition, the strain tolerance (stress divided by elastic modulus) is much greater in AT, indicating that AT can elongate much more than SiC before breaking.

Table 2. Comparison of AT and SiC Properties

	AT-Gen B	SiC
% Porosity	51	58
Pore Size (um)	15	17
MOR (PSI [MPa])	213 [1.47]	1185 [8.17]
eMod (PSI x 10 ⁵ [GPa])	2.10 [1.45]	18.9 [13.0]
CTE (x10 ⁻⁷ /°C)	9	44
Strain Tolerance (MOR/eMod)	1.01e-3	6.27e-4
Cell Density (Cells/in ²)	320	320
Wall Thickness (mil)	12	13
Bulk Density (g/cm ³)	0.74	0.71
TSP (MOR/CTE x eMod)	1127	142

PRESSURE DROP PERFORMANCE

Clean and soot-loaded pressure drop were measured on a series of 4 different AT and SiC samples in 144 mm x 150 mm geometry (5.66" x 6"). The filters were loaded with artificial soot (Printex U – Degussa) by aerating the fine powder into an air stream at a flow rate of ~76 m³/hr. After a specified amount of artificial soot was loaded, each filter was removed, weighed, and placed on Corning's internal pressure drop set-up where the pressure drop was measured as a function of flow rate according to published procedures [8]. The sample was then loaded with more soot and the process repeated until a full curve out to ~5 g/L was obtained. The pressure drop versus soot loading curves for these samples obtained at the highest measured flow rate obtainable in the Corning setup (of 356 m³/hr) are illustrated in Figure 5.

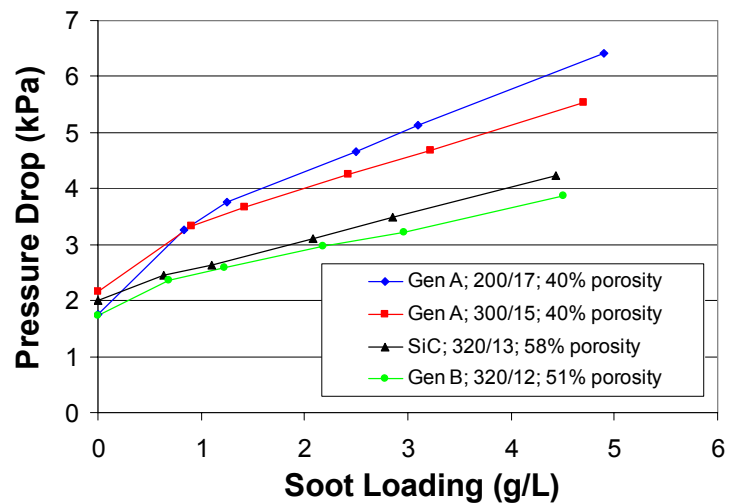


Figure 5. Soot Loaded Pressure Drop Curves for AT and SiC Filters.

Note that according to these test results pressure drop is highly dependent on cell density and web thickness combinations. For example, at the same 40% porosity, the nominal 200/17 AT-Gen A DPF has a higher pressure drop than the nominal 300/15 AT-Gen A filter. Increasing the porosity to 51% while decreasing the wall thickness to 12 mils results in a significant pressure drop decrease for the nominal 320/12 AT-Gen B filter, which has an even lower backpressure than the nominal 320/13 SiC filter with 58% porosity. While lower backpressure is certainly a goal for better engine performance and fuel economy, a filter's ability to survive under the extreme conditions of regeneration will dictate what cell geometry/porosity combinations will be chosen for a given application.

DURABILITY OF ALUMINUM TITANATE FILTERS

In order to verify fitness for use in diesel applications, a series of durability evaluations was conducted on AT-Gen A. These tests included: 1. exposure to engine ash (which contains Fe, P, Ca, Zn, etc.) that can react with some substrate materials to form a eutectic melt or cause densification [1]; 2. exposure to iron and iron oxide (which are common forms of debris in the exhaust system and can react similar to ash); 3. high temperature oxidizing and reducing conditions (which vary as the engine cycles from rich to lean and as soot accumulates on the filter); and 4. acidic solutions (which may result from reaction of SO_x with H_2O in the presence of a catalyst).

Extreme high temperature exposure conditions were chosen to cause failure in the samples in order to establish thresholds. It should be stressed, however, that expected temperature exposure under service conditions is much less severe. Since the peak temperatures observed during regeneration last for periods of seconds, the cumulative time in service at the highest temperatures (assuming ~500 regenerations where only 10% are uncontrolled) is on the order of only minutes. Because there are time/temperature exposure limitations on both catalyst activity and on the sintering of engine ash (temperatures $> 1050^\circ\text{C}$ cause permanent changes in surface permeability due to ash consolidation [1]), the conditions of the tests performed in this study are well beyond conditions expected during practical service conditions.

Ash Stability

Ash stability testing was performed under extreme conditions of 8 hours at 1100°C , 1200°C , and 1300°C with 10% humidity. For this test, actual ash (collected on-engine) is sieved onto several modulus of rupture bars which are broken with the ash contact surface in tension following heat treatment according to the process previously described [1]. No change in strength or preferential failure mode was observed versus untreated parts. As a matter of fact, no reaction was observed with the substrate under any of the above conditions. Cross sections of the samples showed negligible penetration of ash constituents into the bulk of the sample up to 1200°C . After 1300°C , Ca and P had penetrated the top cell wall and some discoloration occurred.

Iron Oxide

Exposure to iron and iron oxide was conducted in a similar fashion to the ash testing. Fine iron oxide (hematite) powder and coarse black iron filings were

applied to the substrate in separate tests. Test coupons were heated in air and soaked for 1 hour at 100°C increments between 900°C and 1500°C . No detrimental reactions with the substrate were observed for any of the test conditions. Even after exposure to 1500°C , the iron material did not penetrate the cell wall. A cross sectional view of an AT cell wall after this exposure is shown in Figure 6.

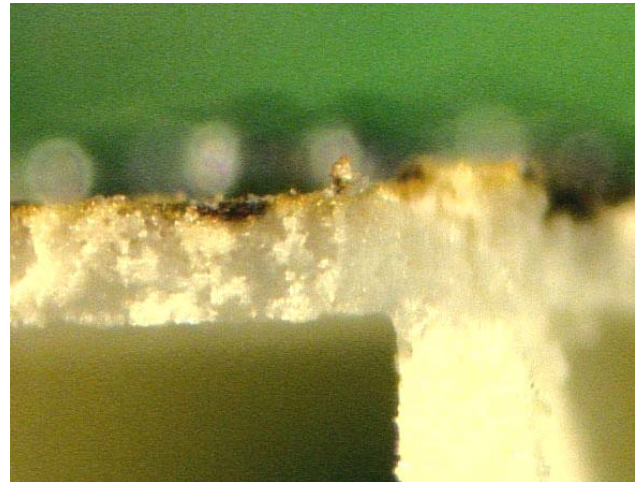


Figure 6. Optical Microscope Cross Sectional View of AT-Gen A Substrate Indicating no Fe Penetration or Reaction Following Exposure at 1500°C for 1 hour.

High Temperature Oxidizing and Reducing Conditions

Exposures of the AT substrate to high temperature under oxidizing and reducing conditions were performed in order to determine the breakdown conditions for the AT-Gen A composition. The aluminum titanate phase, which provides the thermal expansion anisotropy necessary for micro-cracking, is metastable. Given sufficient time, this phase can decompose (Al_2TiO_5 becomes $\text{Al}_2\text{O}_3 + \text{TiO}_2$) at temperatures below 1250°C , and this decomposition results in a higher CTE. The kinetics and thermodynamics of this reaction are strongly influenced by the presence or absence of stabilizing additives [11].

In order to test the AT-Gen A samples under extreme reducing conditions, the filters were loaded with 10g/l of carbon soot and soaked in argon for various temperatures and times to verify fitness for use. These conditions are many orders of magnitude more reducing than the exhaust stream. Samples were also soaked in air to study oxidizing conditions. Results are summarized in Table 2 which also includes expected service conditions: 500 regenerations, 10% uncontrolled.

Table 2. Results of Exposure of AT-Gen A to Oxidizing and Reducing Conditions

	Atmosphere	pO ₂	T (°C)	Time (Min)	Thermal Expansion (CTE)
Reducing	Argon+Soot	10e-20	1200	25	Unchanged
	Argon+Soot	10e-20	1000	600	Unchanged
Oxidizing	Air	0.2	1200	3000	Unchanged
	Air	0.2	1000	6000	Unchanged

Acid Stability

Exposure of the AT substrate to low pH solutions was conducted using sulfuric acid at 80°C for 5 hours. Several solutions at pH's between 7 and 1 were used to determine acceptable conditions for service on engine, and for processing in catalyst coater operations. Commercially available SiC and cordierite filters were also included in this test. Previous studies [12] have shown that pure SiC is unaffected by extreme acidic conditions. However, the product consists of segments which are held together by cement. The authors were not aware of any public disclosure of the performance of these cements in low pH solutions. AT-Gen A showed no degradation in strength under any of these conditions as shown in Figure 7.

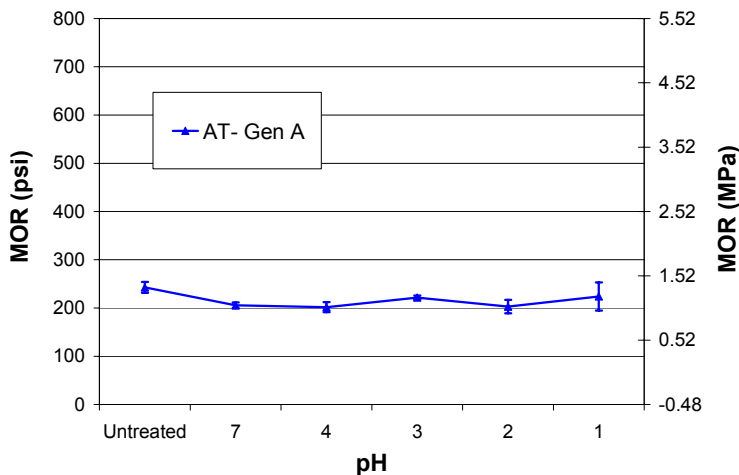


Figure 7. Strength vs. Acid Exposure for AT-Gen A

Durability evaluations of AT-Gen B are ongoing. In fact, as of this publication, AT-Gen B exceeds requirements in the areas discussed above. More detailed results will be published separately.

CONCLUSION

A novel mixed oxide system has been developed for Diesel Particulate Filters. Based on the testing described above, due to the highly microcracked structure and lower thermal expansion, this material has higher

thermal shock resistance than silicon carbide. In addition, internal studies have shown that AT is resistant to chemical attack even when subjected to ash and iron oxides in excess of 1200°C for long exposures. Furthermore, the material seems able to withstand acidic environments that would be expected during the life of the filter. Finally the unique microstructure and 51% porosity of the AT-Gen B composition allows for a better pressure drop than 58-60% porosity SiC while maintaining a higher bulk heat capacity.

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