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Thermal Shock Resistant Alumina Based Diesel Soot Particulate Filters (DPF)

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Thirty years of Diesel soot particulate filter development have enabled ceramic refractory materials to fulfill the requirements of the exhaust system in passenger cars. Silicon carbide wall flow filters currently have the highest market share. However, in automotive applications there is a continual effort to find more cost-effective and reliable materials and systems; an effort in large part enforced by increasing emission standards. A newly developed alumina-based DPF substrate is presented as an economical and ecological alternative.

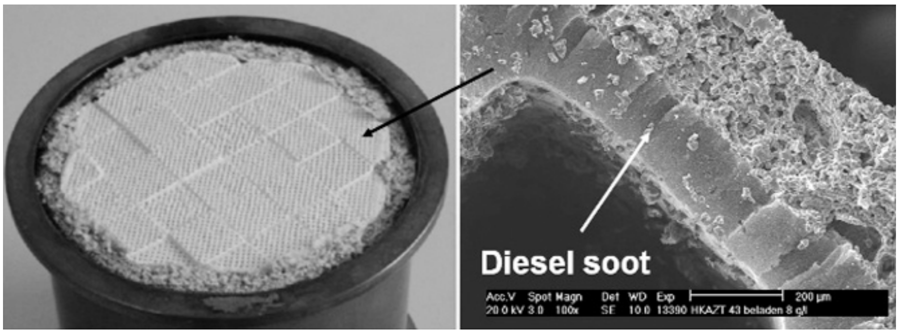

Fig. 1 AZT wall flow DPF prototype (left) and SEM micrograph (right) of a soot loaded channel wall, 100x

1 Introduction

Alumina is one of the most important refractory oxides [1]. Improved thermal shock behaviour as well as thermal cycle stability of fine-grained alumina-based materials have been achieved by equal additions of Mg-PSZ and TiO2 [2]. Specifically a 95 mass-% alumina material with good thermal shock performance has been produced that can be used in advanced secondary metallurgy and continuous steel casting. This refractory not only has improved thermal shock resistance but also has benefits on steel quality due to reduced refractory impurities and carbon pickup [3]. Furthermore, a porous doped-alumina matrix can be applied in hot gas filtration substrates, for example as an alternative material for Diesel soot filters. The thermal, chemical, mechanical and functional requirements of an Al_2O_3-ZrO_2-TiO_2 (AZT)-based filter material for DPF traps were the main focus of the work.

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2 Filtration

For a high filtration efficiency a high surface area and a low pressure drop of gas flowing through the porous material is necessary to get a moderate velocity of exhaust gas passing through the filter. Processing to give over 200 cells per square inch (cpsi) channels in a ceramic body is well known from the extrusion of ceramic honeycomb catalyst carriers [4]. Wall-flow-filter materials are produced by alternate plugging of the channels at the front and back sides, forcing the gas to pass through the porous channel walls. A 250-cpsi-honeycomb filter material based on AZT was produced at the laboratory scale to investigate the suitability of this refractory material for a particle filter substrate. Starting from powder all the manufacturing steps from mixing through extrusion to firing and canning were performed at the IKGB, Freiberg. Fig. 1 shows the particle trap monolith (144 mm) in diameter, which was run in state-of-the-art test procedures of Diesel engine bench tests [5].

3 Regeneration

A DPF device needs a trap for the soot particles and a system to regenerate the trap by removing the particles. Otherwise the particles build up and eventually block the filter so the backpressure rises. The DPF material has to withstand the conditions that occur during thermal regeneration. Soot starts to burn spontaneously at ~ 600 °C; a temperature not often available in the exhaust pipe of an economic Diesel engine. Therefore, it is necessary to raise the exhaust gas temperature by fuel after-injection and to control the regeneration of the filter. Because oxidation of soot is exothermic, there is a local rise in temperature after ignition depending on thermal properties of the filter material as well as the quantity of exhaust and temperature. After regeneration no combustible substances should remain in the filter. Any accumulation of ash leads to increased pressure drop and lower filter capacity so reducing the filter life [5]. A filter material also has to withstand chemical interaction with the ash at high temperatures, which also will occur during regeneration. A filter consisting of a refractory alumina matrix (95 mass-% Al_2O_3) will have superior corrosion resistance in oxidizing environments than SiC. From a cost perspective alumina is also more favourable compared to the state-of-the-art SiC monolith. The newly-developed filter material is made from cheaper raw materials and can be fired at 1600 °C in air in contrast to the re-crystallised SiC material (R-SiC), which is produced by firing shapes derived from a mixture of bimodal SiC powders at temperatures > 2200 °C in a protective gas atmosphere (Ar).

4 Experimental and results

The AZT filter material with 42 % open porosity sintered in air for 2 h at 1600 °C shows a narrow pore size distribution with mean size (d_{50}) of 5 µm at a channel wall thickness of about 0,25 mm. The grain size distribution of the starting powders is the dominant factor controlling the ceramics' porosity. The AZT filter material, which has a 95 mass-% alumina matrix consists of a mixture of calcined (d_{50} = 4 µm) and sintered (d_{50} = 55 µm) alumina powders, which are each doped with 2,5 mass-% fine fractions of TiO_2 and Mg-PSZ. To reveal the differences in porosity caused by the chemical composition the AZT material and a pure Al_2O_3-matrix material were processed under the same conditions. The microstructures were examined using SEM after sintering at 1600 °C (Fig. 2).

The addition of TiO_2 and Mg-PSZ leads to higher shrinkages but also contributes to grain growth. For the doped AZT alumina matrix grain growth dominates leading to a higher level of open porosity. The differences in microstructure as shown in Fig. 2 are purely due to the different chemical composition.

Apart from sintering temperature, the water content and the pore-forming agents (PFAs) of the plastic feed material are other important factors for control of the filter porosity. An important aspect of PFAs is the fact that their burnout products must be environmentally harmless. Additionally, a combination of different PFAs widens the de-bonding temperature range which is optimal for degassing processes. As well as a methylmethacrylate space holder grain (d_{50} = 130 µm) a combination of wheat and methylcellulose was used as plasticizer. The plastic feed material is prepared by directly batching and mixing the raw materials in a high shear auger mixer. In a further step the plasticizers and water were added to the batch to avoid any damage to the organic plasticizers due to long mixing times. Honeycombs 25 mm x 25 mm (200 cpsi – channels per square inch) were extruded with a piston. After drying, the alternate plugging of the channels at the front and back-sides was performed with AZT slurry. After sintering, the honeycomb bricks contained 250 cpsi due to shrinkage of 14,9 %. Then the sintered bricks were glued to a segmented monolith. After a second sinter treatment the monolith was canned to enable its use in engine bench tests. Comparing filtration efficiency, soot loading and regeneration behaviour the AZT showed similar performance than an industrially manufactured SiC filter. The AZT monolith survived regeneration attempts under critical thermal conditions ("worst case" scenario). In this test the engine was stopped after ignition of the soot in a fully loaded trap. Without the cooling exhaust flow temperatures locally rise above 1000 °C and high temperature gradients occur during the ensuing soot oxidation in the filter.

To understand the high thermal shock resistance of the AZT filter substrate based on a 95 mass-% alumina material the microstructure was investigated. The left backscattered electron (BSE) micrograph in Fig. 2 shows a well-distributed light contrast phase in the AZT filter material after sintering at 1600 °C. As well as corundum and baddeleyite X-ray diffraction phase characterization identified $ZrTiO_4$ and $CaZrTi_2O_7$. At high-

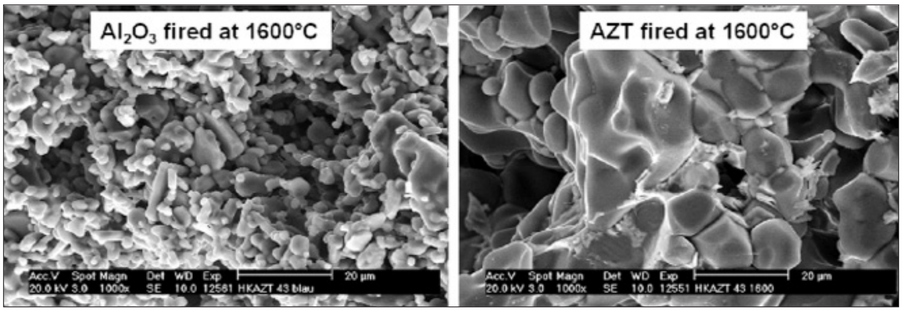


Fig. 2 Different grain growth of Al_2O_3 and AZT sintered at 1600 °C for 2 h, SEM micrograph

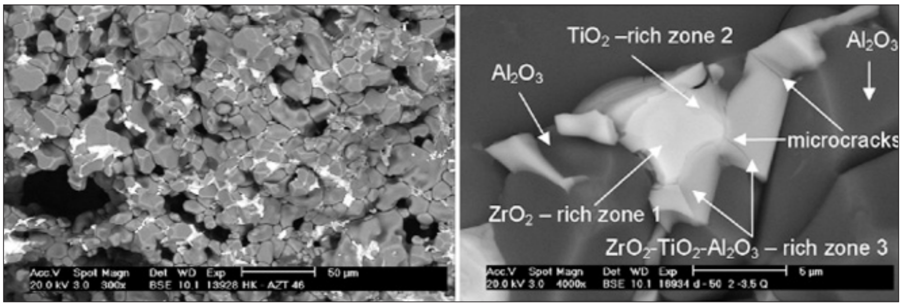
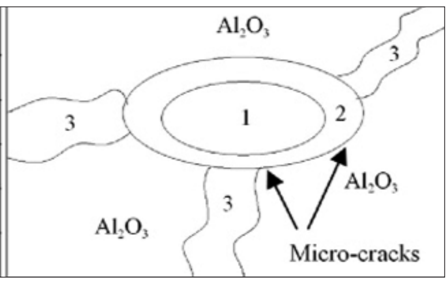


Fig. 3 Microstructure of AZT sintered at 1600 °C for 2 h, BSE micrograph

Tab. 1 EDX analysis of the zones defined in Fig. 3 showing different thermal expansion (right) resulting in a model approach (right) [4]

Material	Al_2O_3	ZrO_2	TiO_2	α
	[mol-%]	[mol-%]	[mol-%]	[10^{-6} /K]
Al_2O_3	100			8,6
Zone 1	15	65	20	-0,6
Zone 2	20	20	60	-4,2
Zone 3	20	40	40	0,5



er magnification besides Al_2O_3 grains three additional zones were identified. EDX revealed zone 1 to be ZrO_2 – rich with < 0,5 mass-% MgO stabilising agent, zone 2 was TiO_2-rich (light grey contrast) and zone 3 was a ZrO_2-TiO_2-Al_2O_3 rich (dark grey contrast).

5 Discussion

The right BSE picture in Fig. 3 indicates that zone 1 has tried to expand on heating but that zone 2 has suppressed zone 1 because of its negative thermal expansion coefficient. "Spring" elements are created in the composite alumina matrix that contribute to the high thermal shock performance during heating and cooling. In spite of the fact that micro-cracks are generated in zone 3 – that additionally contribute to the thermal shock performance – no micro-crack growth is observed after the thermal shock cycling test. The ZrO_2-TiO_2-Al_2O_3-rich area (zone 3) is a re-crystallized melt and acts as a "glue" between the Al_2O_3 grains leading to a high coherence of the structure.

Investigation at the phase composition during sintering reveals that above 1300 °C TiO_2 (as well as Al_2O_3) diffuses into the zirconia lattice leading to destabilisation of the zirconia. A part of the MgO stabilising agent has been removed from the zirconia grain and has been dissolved in zone 2. Through the loss of the stabilising agent the martensitic-like tetragonal to monoclinic polymorphic transformation occurs. Due to the destabilisation and the transformation to the monoclinic polymorph volume expansion occurs that leads to new paths for incorporation of further ions in the zirconia lattice. In zone 3 in several samples Ca has been identified via EDX, with the highest concentrations being equivalent to 8,7 mol-% CaO. Chemical analysis identified this CaO as an impurity in the tabular Al_2O_3 starting powder. Furthermore the durum wheat plasticizer causes a content of 0,1 mass-% ash-producing inorganic salts not low enough to be neglected with respect to the fired ceramic composition. Pure Al_2TiO_5 (ATI) tends to decompose eutectically into Al_2O_3 and TiO_2 from 800 °C to 1300 °C. Because of the Al_2TiO_5-stabilizing impurities, complete ATI destabilization and formation of the ZrO_2-TiO_2-Al_2O_3-rich area (zone 3) is complete for sintering temperatures > 1500 °C.

ATI de-stabilization is accompanied by a lowering of the modulus of elasticity (MOE) measured by three-point bending at 1500 and 1600 °C. The MOE is lowered from 17,7 GPa to 8,5 GPa. A low modulus of elasticity contributes to high rupture elongations (σ/E) as well as to improved thermal shock performance. The rupture elongation for AZT sintered at 1500 °C is 0,0299 %, at 1600 °C it rises to 0,1788 %. The doped material (AZT) presents approximately the same value of the thermal expansion coefficient as the pure alumina material shown in Fig.1.

In addition in spite of the fact that solid-solution areas (zones 1 to 3) with micro-cracks (zone 3) have been incorporated in the matrix no hysteresis of the thermal expansion curve is observed as a function of the thermal cycles.

Different thermal shock tests were performed. The residual four-point bend strength of the AZT sintered at 1600 °C is approximately 65 % of its initial strength after quenching in water (20 °C) from 400 °C. In a further thermal shock test the honeycomb geometries were shocked for 1000 thermal cycles by heating at 800 K/min and cooling at 400 K/min.

The filter substrate survived and no critical cracks were identified. The long-term phase stability was proven in a tunnel kiln test. Honeycomb samples were cycled 200 times from room temperature to 1250 °C over one year. For metallurgical applications the AZT samples with a drill-hole diameter of 15 mm were observed in an impingement test (50 kg iron-melt at 1530 °C). After the test no critical cracks were identified.

6 Conclusion

The high thermal shock resistance of the newly developed filter material based on a 95 mass-% alumina material results from its linear thermal expansion behaviour combined with stable micro-crack formation in the matrix contributing to low Young's modulus of elasticity (MOE). A further reason for the low MOE level is the high porosity of the filter material. The AZT filter material sintered at 1600 °C with 42 % open porosity has low MOE (8,5 GPa). In spite that the thermal expansion coefficient of the Al_2O_3-matrix remains high the low MOE level accompanied by a linear thermal expansion contributes to the thermal shock performance during heating as well as on cooling.

An alumina-based refractory material with Mg-PSZ- and TiO_2-additions covers the mechanical, thermal and chemical demands for a DPF substrate. A wide range of applications for the ATZ material, in particular for hot gas filters, corrosion resistant catalytic converter substrates, as well as for filters and bio-ceramics have been patented (WO 2007/014562 A1).

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