O U R N A L O F

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Solid free form fabrication of silicon carbide cross flow filters

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The paper presents a way to fabricate design prototypes for ceramic diesel particulate cross flow filters by a solid free form fabrication process. Due to the strong undercuts of the structure fugitive wax molds have to be used. The wax mold, which is either produced by rapid prototyping or by stacking milled wax layers, is filled with a ceramic slurry. Gelcasting, a ceramic forming technique for complex shapes, was used in combination with the fugitive wax molds to produce monolithic cross flow diesel particulate filters (DPF). The gelcast cross flow filters have dimensions from $20 \times 30 \times 28$ mm³ to $90 \times 90 \times 40$ mm³ and wall thickness from 0.4 to 1 mm. The material used is recrystallized silicon carbide (RSiC), because it has an inherent porosity, good thermal shock resistance and a non-shrinking sintering behavior. Furthermore the binder removal and the sintering are discussed.

Key words: Gelcasting, DPF, RSiC, Ceramics, Rapid Prototyping.

Introduction

Diesel particulate filters (DPF) are of great interest for the automotive industry because the restriction concerning the emission of substances harmful to the environment is getting tighter. Although the diesel engine is more efficient than the Otto engine regarding fuel consumption and therefore produces less carbon dioxide, the emission of particulate matter (PM) and nitrogen oxides (NO_x) is significantly higher. Due to the potential health risk of PM and NO_x the European Union, the United States and Japan are the leading countries restricting the level of emissions. While current regulations on PM could be reached by most car manufacturer by a good motor management, future regulations will make the usage of DPFs necessary. The German car industry will use DPFs on all diesel cars by 2009 [1]. At that time the Euro 5 regulation will come into force, which will restrict the NO_x emission to 180 mg/km and the PM to 5 mg/km. This will be further tightened by the Euro 6, which will enforce in 2014 a decrease in the limit of NOx to 80 g/km and leave the limit for PM the same, but will also implement a number based standard for PM [2]. The European regulations concerning heavy duty vehicles are usually referred to as Euro I to Euro V. The current values for Euro IV are 3.5 g/kWh for NO_x and 0.03 g/kWh for PM. For Euro V which will come in 2008 the NO_x will be reduced to 2.0 g/kWh and the PM limit will stay constant [3]. As mentioned earlier these regulations will make the usage of DPFs for passenger cars as well as for heavy duty

vehicles inevitable, because there is a trade-off of NO_x and PM. As NO_x is reduced the emission of PM will raise.

Diesel Particulate Filter

DPF were invented in the early 1980s and are based on honeycomb structured catalytic converters made of a porous ceramic. Filters should have a good filtration efficiency, a low pressure drop, good regenerability and a high resistance to thermally induced stresses. Porous ceramics are, due to their refractory nature and ability to control their porous microstructure, suitable materials for DPFs [4]. Silicon carbide (SiC) has been the preferred ceramic filter material, but others like cordierite, mullite and aluminum titanate are already established or are emerging [1].

DPFs can also be made of metal, but ceramic DPFs are more advantageous concerning weight, coefficient of thermal expansion and high temperature and corrosion resistance. Metals have a higher strength and a higher thermal conductivity. Filters can be made of sintered powders, fiber felts or knitted fibers and open cell foams [5]. SiC is still the preferred filter material due to its high stability under real world operating conditions. It is in contrast to other filter materials highly resistant to heat, it has a high thermal conductivity, which is important for a good temperature distribution during regeneration and a high specific heat, which holds down the regeneration temperature. Furthermore SiC shows a minimal reactivity to chemical compounds in the exhaust gas and has a high mechanical strength, which helps to withstand the stresses and vibration during canning and driving [6]. But the coefficient of thermal expansion is rather large, which leads to thermal stresses due to temperature gradients. This might lead to a cracking of the filter and to a decrease in filtration efficiency, but this crack problem can be handled

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by using split-type DPFs [7]. However, nevertheless the choice for the DPF material has to be compatible with the regeneration strategy, the application and the economically viability [4]. Ceramic filters are usually produced in a honeycomb shape by extrusion and alternate plugging of the channels on the front and back side forces the gas to flow through the porous walls, which is why these filters are referred to as wall flow filters. They work as diffusion filters, which means that the small particles attach themselves to the porous wall or diffuse to the soot cake, which has been built up by previous particles [7].

These particles, which are between 5 µm and 50 µm in size, are organic ashes like solid carbon, absorbed hydrocarbons, sulphur containing particulates and also inorganic oil or fuel-based residuals as well as motor wear [4]. The organic ashes have to be burnt off from time to time depending on the regeneration mechanism (For further information on regeneration mechanism see [7]) and on the particulate loading, which is approximately every 400 to 1,000 km. This will lead to hundreds of regenerations for passenger cars or thousands of regenerations for heavy duty vehicles, because they have to survive typically for more than 200,000 km or for > 500,000 to 1,600,000 km respectively [4]. The inorganic ashes are collected in the rear end of the plugged channel of the extruded honeycomb shaped DPF (see Fig. 1). The accumulation of the inorganic ashes reduces the effective filter volume gradually from the rear side, which causes first a rise in pressure drop and finally a complete breakdown of the filter [7]. This is not problematic for passenger cars because they have a lower level of ashes and newly-developed filters (e.g. Ibiden's Octosquare) have a lifetime of about 250,000 km [5]. Heavy duty vehicles emit a higher level of ashes and their lifetime should be at least more than 1 million kilometre.

Cross Flow Filters

An alternative concept to solve the above mentioned issues is a cross flow filter, where the outlet channels are orthogonal to the inlet channels. The inorganic ashes are



Fig. 1. Scheme of a honeycomb DPF



Fig. 2. Scheme of a cross flow filter with ash-chamber.

collected in an ash-chamber, which can very easily be removed. A design of a cross flow filter shown in Fig. 2 is derived from the Patent WO 2005/033477 A1 [8].

The cross flow filter can be made out of the same material as the extruded filter and will have similar material properties. It is still a wall flow filter, where the same regeneration mechanisms can be applied. Simulations show that the inorganic ashes will be collected in the ash chamber, which should be removable like a vacuum cleaner bag. Because the filter is not clogged anymore from the backside, the lifetime of the filter is not dependant on the filling level of the ashes. The inorganic ashes can be removed via the ashchamber and therefore the volume of the filter can be reduced, because the entire ashes have not to be stored over the whole lifetime. The simulations show furthermore a better distribution of the temperatures over the whole cross section during regeneration due to the orthogonal outlet channels.

First attempts to implement cross flow filters for diesel exhaust have been undertaken by Takesa et al. [9]. This filter is now produced by Asahi Glass in Japan and is made of a laminate of extruded cordierite plates, but it is only for stationary use. The cleaning of the filter is done by a reverse jet flow system [10].

Fabrication method for cross flow filters

Cross flow structures are complex in design and therefore they cannot be fabricated in one part by classical ceramic forming techniques. They can be fabricated by tape casting and laminating several wavy layers, but this leads to the problem of delamination and no monolithic cross flow filters can be produced by tape casting. Another possibility is to structure the ceramic filter directly with rapid prototyping (RP). A suitable process is 3D printing, where a binder, which is spread similar to an ink-jet printer principle, selectively bonds the powder. The powder bed is lowered by the layer thickness and new powder is spread on the bed after a layer is completed. After all slices have been built the part is cured and the loose powder is shaken off. Finally the part is debinded and sintered, which results in a porous body [11]. Ceramic cross flow filters have been produced by 3D printing and tested, but are not commercially available [12]. Another RP-process would be stereolithography with ceramic filled resins, which are photosensitive and are cured by laser light. Since the cure depth is controlled by the particle size and especially by the refractive index difference between the ceramic and the resin various ceramics results in different cure depths [13]. Cross flow structures can also be cast, as was shown by Vaubert et al. [14] at the Oak Ridge National Laboratory, USA. They developed a fabrication process for a monolithic cross-flow hot-gas filter for pressurized fluidized bed combustion (PFBC) and integrated gasification combined cycle (IGCC) using gelcasting technology. The shape of the channels are either rectangular or rounded, so that the part can be removed from the mold, which is made of anodized aluminum [14]. For the production of the filter depicted in Fig. 2 none of the above mentioned methods are suitable, if the part should be produced as a monolith and if the production should be on a larger scale for industrial production. Since hard tools are used by Vaubert et al., undercuts, as they are shown in Fig. 2, can not be realized, because the part cannot be removed from the mold. This cross flow filter needs to be made by the lost mold method, because the constant wall thickness of the hexagonal inlet channels causes undercuts in the outlet channels. Hence, gelcasting technology has to be combined with a lost wax mold, which can be melted off to produce the required undercuts [15]. Different wax mold fabrication processes have been evaluated and compared to direct fabrication processes such as 3D printing and stereolithography. The molds can either be produced by a RP process, which uses low melting wax or the mold can be produced by stacking independent wax layers over ond another. The individual wax layers can be produced by either milling or injection molding. As can be seen in Fig. 2 this cross flow filter has two different channel shapes. Each layer of channels does not intersect with one another. It is therefore possible to fabricate the mold for this cross flow filter layer by layer. The estimated lead times and the build speed of the various building strategies are depicted in Table 1. The numbers were gained from various data sheets and by our own measurements. The mold fabrication processes used are described in more detail in the following sections.

The direct methods seem to be appropriate for prototypes, but their low build speed is unusable for industrial manufacturing on a large scale. Furthermore the removal of the unbound powder for the 3D printing process will be critical if the channels are narrow and long. Attempts to fabricate silicon carbide filled resins by stereolithography

Table 1. Lead time and build speed of different build strategies

Build Strategy	Lead Time	Build Speed
Indirect Methods		
Solidscape's wax-printer	1 h	1-10 cm ³ /h
Milling	3-5 days	20-200 cm ³ /h
Injection Moulding	4-6 weeks	10 000 to 100 000 cm^3/h
Direct Methods		
3D Printing	1 h	20-500 cm ³ /h
Stereolithography	1 h	20-300 cm ³ /h

have failed, because the photosensitive resins could not be cured due to the high absorption of the light by the ceramic particles.

Since the build speed is crucial for the implementation of a production on a large scale gelcasting in combination with the fabrication of the mold by injection molding seems to be the only feasible process, but it is not industrially implemented yet. Since until now no monolithic cross flow filter for DPF application has been produced by this novel approach different designs should be evaluated and different molds will be needed. Due to the fact that the production of an injection mold takes a long time and that geometrical alterations as well as the production of the mold itself are very expensive different ways have to be found. For the very first attempts molds were produced by the Solidscape's wax-printer. In a second step larger wax molds were made by computerized numerical control (CNC)-machining.

Experimental

Fabrication of the Mold via Rapid Prototyping

Complex geometries can be produced via RP by depositing material layer by layer. The model is built by the RP machine directly from computer aided design (CAD) data. Since an additive process is used every geometry can be built. There are a couple of RP techniques, but not all of them can produce a mold for the filter depicted in Fig. 2.

Very advantageous is a RP technique which uses a soluble support material for holding up the undercuts of the build material, because the support of internal overhangs can be removed very easily. Processes such as laser sintering would fulfill this requirement, but the loose, unsintered powder, which supports the undercuts, cannot be removed if gaps are very narrow. Furthermore most RP-materials have no or a very high melting point, but for the combination of RP with gelcasting a low melting build material (< 100 °C) is very important. Higher melting mold materials might lead to breakages of the gelcast part due to the shrinkage of the gelcast part during drying. At the moment the Solidscape wax printer is the only RP-technique on the market, which fulfills these requirements. Because of its high accuracy and



Fig. 3. Cracks on curling on the mold made with the Solidscape wax printer due to thermal stresses.



Fig. 4. Mold made with Solidscape's Benchtop.

good surface finish this system is used in the jewellery and medical industry for the production of patterns for investment casting [16]. This RP-process is relatively slow compared to other RP-techniques, hence only small parts should be built with that process. For larger parts the build time becomes prohibitively high. Furthermore larger parts ($5 \times 5 \text{ cm}^2$ base) with fine structures tend to break and curl due to thermal stresses (see Fig. 3.).

These stresses can be minimized by placing the model in a certain position in the build chamber and by increasing the cooling time between two slices. The edges of the model should not be parallel or orthogonal to the lateral axis, they should have an angle of 45° to these axes. Furthermore the model should be tilted in both possible ways by at least 3° to 5° .

The process steps for building a mold with the Solidscape wax printer are similar to any other RP-technique. A CAD-model of the mold is needed and the software slices the CAD model into layers and calculates the build parameters. The RP-machine builds up the model by jetting build and support material droplet by droplet and layer by layer. After the building process is finished the



Fig. 5. Concept model of a SiC-DPF cast in a RP mold. The model has a wall thickness of 0.5 mm and an inlet cross section of 3.8 mm^2



Fig. 6. Concept models of a DPF cast in a RP mold. The model has a wall thickness of 0.4 mm and an inlet cross section of 2 mm².

support material has to be dissolved in a mineral oil bath. Special care has to be taken to avoid the formation of cracks. A finished mold with already dissolved support wax, which was built by the Solidscape wax printer BT612 is shown in Fig. 4. With this kind of technology highly complex molds can be produced and the geometry can be easily altered.

Two concept models of a DPF with different size and wall thickness cast in a RP mold are shown in the following pictures. The model in Fig. 5 has a total volume of $25 \times 36 \times 65$ mm³ and a constant wall thickness of 0.5 mm. The hexagonal inlet channels have a cross section of 3.8 mm² (104 cpsi). The model in Fig. 6 is $31 \times 24 \times 28$ mm³, its wall thickness is 0.4 mm and the cross section of the inlet channels is 2 mm² (172 cpsi). Cells per square inch (cpsi) is usually used for characterizing the total number of channels for extruded honeycomb filters. Since this compromises both Space missing: inlet- and outlet channels of the extruded filter, the cell density for CFF is doubled for a better comparison.

Fabrication of the Mold via Milling

In order to increase the overall build speed, there was a need to search for other methods to produce bigger parts. For the first prototypes a process similar to Mold Shape Deposition Manufacturing (Mold SDM) seems to be an apropriate method. Mold SDM is an additive-subtractive layer manufacturing process, where a CNC-mill is used to shape each layer [15]. The individual layers were stacked after milling. This is a very effective technique to produce such prototypes because hardly any tool costs occur.

Two different shapes with a length of \sim 90 mm of the milled layers and a resulting wall thickness of the filter of 0.6 mm are shown in Fig. 7.

In Fig. 8 a detailed picture of the wax layer of the inlet channels is shown.

A filter made by milling and stacking of two different kinds of wax layers with a wall thickness of 1 mm, a volume of $90 \times 90 \times 40$ mm³ and an inlet cross section of 32 mm³



Fig. 7. Milled wax layer for the inlet (top) and outlet channels (bottom) with a resulting wall thickness of the filter of 0.6 mm.

is depicted in Fig. 9.

Fabrication of the gelcast parts

Gelcasting is a slurry-based forming technique and was first patented by Janney and Omatete in 1991 [17] : a low viscosity slurry, consisting of ceramic or metallic powder, an aqueous or non-aqueous solvent, dispersant and two organic monomers, is poured into a mold and polymerized in situ. The polymerization is triggered by a free radical initiator and a catalyst, thereby forming a firm polymer-solvent gel matrix which immobilizes the particles in the desired shape of the mold. After drying the parts may be machined then they are debinded and sintered [18].

Compared to slip casting and powder injection molding gelcasting offers several advantages. There is no need for



Fig. 8. Detailed picture of the milled wax layer A filter made by milling and stacking of two different kinds of wax layers with a wall thickness of 1 mm, a volume of $90 \times 90 \times 40 \text{ mm}^3$ and an inlet cross section of 32 mm² is depicted in Fig. 9.



Fig. 9. Filter with a wall thickness of 1 mm and an inlet cross section of 32 mm²made by milling and stacking.

expensive tools, gelcasting can therefore be used for the production of prototypes. The part obtained has very homogeneous material properties and can be machined very easily in the green state. In comparison to powder injection molding the binder content is very low (3-5 wt%), and therefore the binder burnout is an uncritical step. Parts made by gelcasting can be more complex than those made by powder injection molding or slip casting [19].

Gelcasting molds are in contrast to slip casting nonporous molds and they can be fabricated from a wide range of materials. The mold can be made of metals or even glass, plastics and waxes, because it is not exposed to high stress [17]. The possibility to use wax as a mold material, allows the fabrication of very complex parts because the wax can be melted off. The melting point of the wax has to be between 80 °C and 100 °C, because a lower melting point could lead to distortion of the mold during the heating for polymerization and a higher one could destroy the part during dewaxing [15]. Both types of molds produced by either RP or stacking the milled layers where filled with the same slurry, which consists of the components shown in

 Table 2. Components of the slurry

Amount	Material
5 g	gel forming monomer (Methacrylamide)
15 g	cross linking monomer (N,N'-Methylenebisacrylamide)
50 g	deionised water
0,5 g	dispersant (Tetramethylammonium hydroxide)
200 g	SiC (mixture of fine and coarse grain)

Table 2.

After ball milling for a least 12 h the slurry was de-aired in a vacuum and the initiator (ammonium persulphate) and the catalyst (N,N,N',N'-tetramethylethylenediamine) were added. The slurry was de-aired again and then the mold was filled under vacuum. The filled mold was then placed in a climate chamber at 60 °C and very high humidity, where the polymerization of the monomers formed a gel-like green body. By increasing the temperature the wax was melted off and the part could then be dried very carefully.

For evaluating the casting properties, the slurries were examined regarding their rheological properties. The measurements of the slurry viscosity depicted in Fig. 10 were done by a plate-plate system at 20 °C with a gap of 0.2 mm (Paar, Physica MCR 300). It can be seen that the viscosity is very low at higher shear rates, but increases significantly at lower shear rates.

Binder removal and sintering

Compared to powder injection molding the binder removal of gelcasted parts is an uncritical step due to a low binder content (3-5 wt%). The more critical step is the above mentioned drying of the body. The burnout characteristics of the binder was studied by thermal gravimetrical analysis (TGA) using a TA Instruments TGA 2050 system. The polymerized binder alone and the gelcast samples were analyzed in air and nitrogen. Additionally the fine SiC powder ($d_{50} = 0.8 \mu m$) was heated up in air to see if there are any oxidation processes of SiC to SiO₂.

In Fig. 11 the results of the TGA analysis are depicted.



Fig. 10. Viscosity of the SiC-slurry.



Fig. 11. TGA analysis.

The weight gain of the fine grain SiC powder in air is shown in Fig. 11a. It can be seen from both the weight gain and the first derivative of the weight with respect to temperature that the oxidation process starts above 600 °C at a heating rate of 1 Kminute⁻¹, which is comparable with the real debinding process. A negligible amount of SiO₂ is generated below 600 °C. More important than the suppression of the oxidation of SiC is the elimination of the elemental carbon. The incomplete elimination of the elemental carbon in nitrogen is shown in Fig. 11c, where the pyrolysis of the pure polymerized binder is depicted. A residue of 3%, which is mainly elemental carbon, is left in the nitrogen atmosphere at a temperature of 600 °C after a hold time of one hour. In contrast the residue in air is only 0.5%. The same can be seen in Fig. 11b, where the debinding of the green part is simulated. A constant weight is reached at 600 °C in air and nitrogen, whereas the residue left in nitrogen is higher than in air. Therefore the debinding should be conducted in air rather than in an inert atmosphere to guarantee the complete elimination of the elemental carbon.

During sintering of SiC-powder two competing sintering mechanisms -a non-shrinkage and a shrinkage mechanismoccur. In the case of solid sintered SiC (SSiC) the presence of elemental carbon is inevitable to suppress the nonshrinkage consolidation mechanism, whereas for the zero shrinkage behavior of recrystallized silicon carbide (RSiC) elemental carbon is detrimental. The RSiC material utilized consists of a bimodal grain size distribution of SiC powder. The fine grain powder undergoes an evaporation-consolidation mechanism which is described in detail in [20] and [21]. This process will not be finished as long as there are still some fine grain particles. These evaporated particles Solid free form fabrication of silicon carbide cross flow filters



Fig. 12. SEM images of sintered RSiC specimens with coarse grain particle sizes of 17 μ m (top) and 35 μ m (bottom).

consolidate on the coarse grain particles and this leads to the grain growth of the coarse particles, which fuses them together. Although the bimodal particle distribution leads to a high packing density in the green state, this non-shrinking sintering mechanism, where no further densification of the body occurs, leads to an inherent open porosity of the body. This predominant sinter mechanism can be suppressed by the presence of only a small amount of elemental carbon. Hence, all the organic binder has to be removed prior to sintering, to ensure a non-shrinkage consolidation mechanism.

Material properties of RSiC

For DPF applications the inherent porous structure and its good thermal-shock resistance RSiC is favorable. Furthermore the pore size distribution is very narrow and the pore size can be adapted very easily by the variation of the particle size of the coarse grains. In Fig. 12 two images takes with a scanning electron microscope (SEM) (Philips XL 30) with the same magnification of sintered RSiC specimens with coarse grain particle sizes of 17 and 35 μ m are depicted. These SEM image are taken from a fracture surface.

The flexural strength of sintered specimens which decreases with increasing particle size from 60 ± 5.2 MPa to 45 ± 4.8 MPa, is shown in Fig. 13. Although the coarse grain size doubles, the porosity decreases slightly from 39% for the smaller grain size to 37.6%. The average pore



Fig. 13. Pore size distribution and flexural strength of sintered RSiC specimens with coarse grain particle sizes of 17 and 35 μ m, respectively.

radius is nearly doubled from 4.6 μ m to 9 μ m and the pore size distribution for both particle sizes is very narrow as shown in Fig. 13. Sintering was conducted at 2,200 °C in an argon atmosphere and the analysis of the porosity was done by mercury intrusion porosimetry (Porotec Pascal Porosiometer 440).

The flexural strength was measured with an universal testing machine (MTS Synergie 200) in a 3-point bending test at 25 °C with a span width of 20 mm and a cross head speed of 0.5 mm/minute. The specimen were tested "as fired", without chamfering and their size was 3x4x > 25 mm³.

Conclusions

Gelcasting is an appropriate production technique for manufacturing cross flow filters. In this paper different mold fabrication techniques have been evaluated for the production of prototypes. Concept models of DPFs with different wall thicknesses down to 0.4 mm and different dimensions have been produced. Binder characteristics and oxidation behavior have been analyzed to determine the burnout characteristics for the debinding process. It is recommended to debind in air to eliminate all elemental carbon, because the sintering behavior of RSiC is very sensitive to any residue of elemental carbon. The subsequently sintering should be conducted under argon with temperatures up to 2,200 °C. It could be shown that the pore size distribution is very narrow and that it is easily adaptable by selection of the coarse grain particle size. Mercury intrusion porosimetry was conducted to determine the porosity and the average pore radius. The examination of the fracture surfaces and the flexural strength testing show a good bonding of the coarse grains, which results in a high flexural strength.

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