EXPERIENCES WITH SOL-GEL BONDED HIGH POROSITY ALUMINA FIBER MATERIALS FOR FILTER APPLICATIONS

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ABSTRACT

High porous alumina fiber structures appear promising for hot gas filtration in particular for diesel particulate traps. For this purpose, however, a method is required for manufacturing of stable shapes resistant to the blow-out by the gas flow. The sol-gel-process was expected to be the best suited method for fiber bonding to provide the required stability.

The main tasks of the development-work were a uniform isotropic fiber-distribution, the adaptation of the sol-gel-process to the application, and the deliberate synthesis of the gel-derived alumina bonding phase.

The appropriate fibrous structure was obtained by a repeated filtration of sol/fiber suspensions. The properties of the ceramic binder were adapted by concentrating the sol and/or adding aluminas or aluminium hydroxides.

Testing of prototypes with optimized structures has shown, however, that the stability of the structure decreased after thermal load. The thermal fatigue of α-Al_2O_3 is assumed to be responsible for this failure.

INTRODUCTION

Open-pore structures of heat-resistant ceramic fibers are promising candidates for applications in hot-gas filtration, for example in diesel particulate traps, provided that they can be stabilized by the use of heat-resistant binders without loss of porosity.

For these applications such a composite would have to exhibit not only heat resistance but also thermal-shock resistance and corrosion resistance. In tests so far been reported in the literature, in which unspecified ceramic fiber products were used as exhaust filters, a particle collection efficiency of up to 90 % has been achieved with an acceptable exhaust back pressure [1]. On the other hand, attention was drawn to the insufficient durability of these products. Thus with fiber filters of short Al_2O_3 fibers (Saffil) a collection efficiency of only 45 % was achieved in the same test owing to the blow-out of fibers [2]. A positive finding proved to be the good regenerability of the filters, i.e. the case with which the deposited soot can be burnt off. By contrast, after regeneration cordierite honeycomb filters repeatedly showed cracking [2,3]. Another advantage of fibers which has a positive influence on regenerability is their low heat absorption during soot burn-off [4]. However, the disadvantage of thermal stresses arising from the low thermal conductivity of the material during burn-off was also pointed out. This probably holds true only if the fibers are packed so tightly that they act as a surface filter, resulting in a pronounced anisotropic temperature curve during burn-out. This was most likely true of the case described in [4] as well.

The chief aim in developing a ceramic-fiber-based filter were therefore to obtain a system which, in addition to good high-temperature characteristics, also exhibits high porosity and a low fiber density with sufficient stability of the fiber structure to resist the blow-out effect of the flowing gas.

The advantage of the sol-gel process for introducing a bonding phase is that the fibers can be impregnated with a liquid medium, so that the homogeneity and quantity of the deposit can be precisely controlled. The main prerequisite for the successful development of a depth filter was the realization of an isotropic fiber distribution. A mean pore diameter of 50 µm was regarded as advantageous. In addition, it was considered essential to synthesize a gel

Mat. Res. Soc. Symp. Proc. Vol. 121. ©1988 Materials Research Society

with a high solid phase content that underwent minimal cracking and shrinking during firing but which nevertheless exhibited good impregnation behaviour. The specific strength of the resulting ceramic bonding phase would have to meet stringent requirements. For this purpose, minimal residual porosity and uniformly small particle size were essential.

EXPERIMENTAL PROCEDURE

Saffil fibers (ICI) with a mean fiber diameter of 3 µm were used as a fiber material. The bonding phase employed was an Al_2O_3 gel synthesized from Al-sec-butylate by the method described in [5], which after firing results in Al_2O_3. In order to increase the solid phase content beyond the value of 2.4 % (α-Al_2O_3) described in the literature [5,6,7], an attempt was made to greatly reduce the solvent (H_2O) and achieve additional enrichment of the solid phase by adding boehmite AlOOH, α-Al_2O_3-powder and Al-salts $Al(NO_3)_3$, $AlCl_3$. Care had to be taken to ensure that a viscosity was achieved after blending that was suitable for the subsequent impregnation process. The particle size of the resulting oxide-ceramic bonding phase was influenced by seeding with γ-or α-Al_2O_3 (1-10 % by weight). An Al_2O_3-gel reduced to one third of the original solvent content, to which 5 % (by weight) glycerine [8,9] and up to 5 % (by weight) plastifier, e.g. polysaccharides or methylcellulose, were added as drying control chemical agents (DCCA) to reduce the cracking tendency by drying, was adjusted to a viscosity of 300 mPa·s. Stirring in the Saffil fibers resulted in a suspension with 10 g/l fibers and a viscosity of 100 mPa·s. The fiber length was substantially shortened by this procedure ($\leq$ 5 mm).

By means of pressure filtration of the fiber-gel suspension in a continuous process (repeated suctioning), self-supporting tubes with a length of 600 mm and a wall thickness of approx. 10 mm were produced from a sol-gel-reinforced fiber structure. In order to keep the fibers suspended, air was blown into the vessel from below. The subsequent drying and firing process was performed in stages under controlled atmospheric and temperatur conditions. It was possible to control the volume shrinkage to the extent that only microcracks (see Fig. 1) occurred.

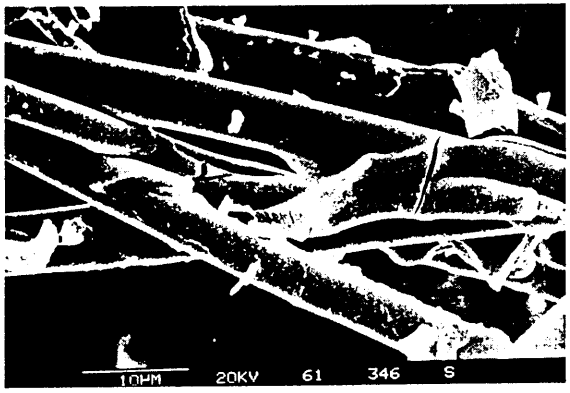

Fig. 1 Al_2O_3 fiber composite before the filter test.

The test filters thus produced were tested with respect to the deposition rate, the pressure drop in the exhaust-gas stream and mechanical stability in a cyclical engine test with an MAN underfloor engine D 2566 UH 200. The following measurements were taken: the smoke number with a Bosch indicator, an exhaust-gas analysis with an FTIR spectrometer and the particle mass.

Reduction of the solvent in the gel batch resulted in an increase in the solid phase content from 2.4 % to 5 % Al_2O_3. The addition of boehmite or Al_2O_3-powder to the gel increased the solid phase content to 12 %. The addition of up to 20 % (by weight) boehmite powder with respect to Al_2O_3 from alkoxide resulted in a steady decrease of the total gel volume. The addition of more boehmite resulted in the gel volume increasing again. Increasing doses of boehmite or α-Al_2O_3-powder were associated with increased viscosity with the result that the gel was no longer suitable for the subsequent impregnation process. Also, the addition of up to 100 % (by weight) $Al(NO_3)_3$ or $AlCl_3$ proved unfavorable owing to crystallization of the salts during firing. Seeding the Al_2O_3 gel with α-Al_2O_3 [10] in the range of 1-10 % (by weight) with respect to the total gel weight yielded an extremely fine-grain structure after firing (mean grain size 0.05 µm). Figs. 2 and 3 show this effect. Seeding experiments with γ-Al_2O_3 have not produced this pronounced fine-grain structure of the final ceramic product.

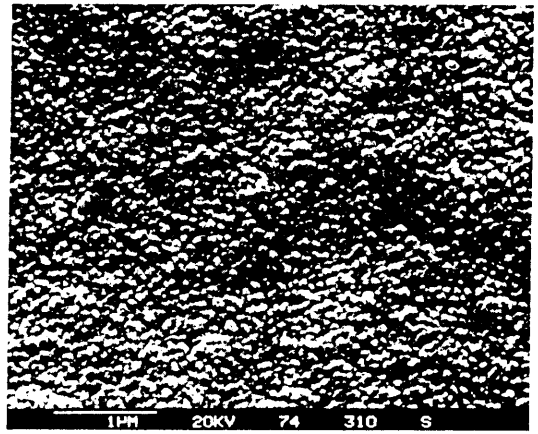

Fig. 2 Structure of an Al_2O_3 sample synthesized by the sol-gel process with seeding (5 % by weight Al_2O_3 seeds).

As a further effect of the addition of Al_2O_3 powder, DTA measurements showed an increase in the γ-Al_2O_3/ α-Al_2O_3 transformation-temperature from 1000°C to 1200°C during firing. In this respect γ-Al_2O_3 was also effective. The addition of boehmite powder, by contrast, resulted in an increase of the transformation-temperature.

The increased solid phase content and the reduced microporosity led to strength values of 1 N/mm² for the fiber composite.

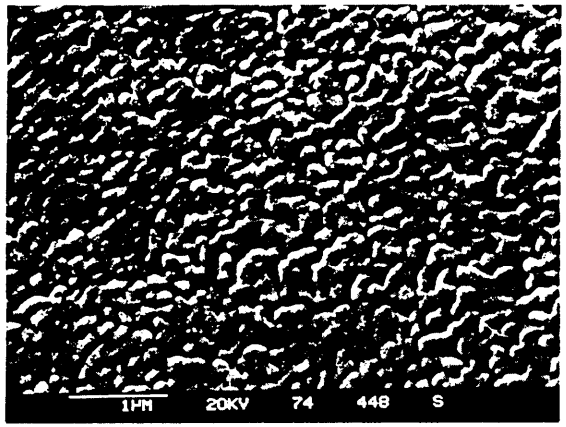

Fig. 3 Structure of an Al_2O_3 sample synthesized by the sol-gel process without seeding.

The particle collection efficiency of the filter was found to be 97 % with a simultaneous pressure drop of 23 mbar and a flow rate of 100 m^3/h. During the test a sudden fall in the pressure loss was observed, indicating leakage of the filter. Upon removal of the filter, partial detachments of the fiber structure and macroscopic cracks were seen. Subsequent examinations have shown that the alumina bridges between the fibers ruptured (Fig. 4).

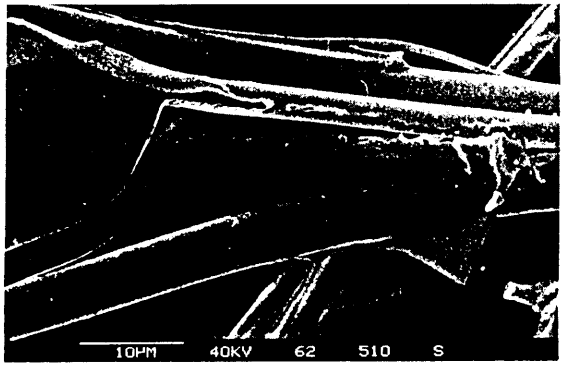

Fig. 4 Al_2O_3 fiber composite after the filter test. Increased cracking tendency is apparent.

Further weakening is caused by stratification of the structure perpendicular to the gas flow during pressure filtration. The low density perpendicular to the layers favors cracking.

The reason for this finding lies in the unfavorable thermal and mechanical behaviour of α-Al_2O_3 as a bonding phase. Thus the resistance to thermal cycling proved too low and the interfacial bond strength between the fibers and the bonding phase too great.

CONCLUSION

The particle collection efficiency of up to 97 % measured in the initial test phases has demonstrated the efficiency of a gel-bonded ceramic fiber structure for filter applications. However, the strength of the composite so far achieved is insufficient for use, for example, in the filtration of engine exhaust gases. A substantial increase in strength with the fibers used is unlikely to be possible. A solution may be found in structural measures, e.g. applying the fiber composite to a coarser porous carrier.

Embedding the fibers in a ceramic "matrix" with the sol-gel process has proved to be a promising approach. The problems associated with marked shrinkage can be largely overcome by enrichment of the solid phase, the addition of suitable DCCA's and optimum drying and heat treatment. By means of selective seeding of the initial gel a uniform fine-grain structure of the resulting ceramic bonding phase is retained.

The choice of alumina as a bonding material, however, is probably inappropriate owing to the insufficient resistance of the substance to thermal cycling. An improvement in this respect will be attempted through the development of mullite-yielding gels.

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