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The upshot of nanospheres oxidation on strength crack in diesel particulate filter porosity sinters

At the end of 2004, a European automobile manufacturer equipped more than 1 million diesel engine passenger cars with pure SiC diesel particulate filters. High porosity ceramics and ceramic-metal composites are now widely applied in a number of fields. The DPF may be manufactured from different materials i.e cordierite, silicon carbide. Applying porous DPF in Diesel has been considered a promising concept in approaching a near-zero emission system. It takes full advantage of PM geometry and material characteristics to realize homogeneous combustion, therefore reduces significantly the emission of PM, under all operating conditions. In order to achieve the material properties, microstructure control philosophy has been kept as the principle to optimize the character of material to satisfy the necessary real diesel emission control. The DPF consists of narrow channels which are blocked on one side. The first segment of DPF consists of diesel catalyst filter DOC, which is made of silicon carbide sinters and porous Ti_4O_7 . We investigated porous ceramic structure, under load condition – thermal shock, which can lead to fracture of ceramic material and damage to the noble metal-catalyst-Pd-Ru₃, which is deposited on high porosity Ti_4O_7 -SiC structure.

Wpływ tlenkowych nanosfer na kruche pękanie nośnika filtra cząstek stałych

W roku 2004 europejski przemysł motoryzacyjny wprowadził na rynek ponad 1 mln samochodów osobowych z silnikami ZS wyposażonymi w filtry cząstek stałych zbudowane z SiC. Materiały ceramiczne o dużej porowatości i kompozyty ceramiczno-metalowe znajdują coraz częstsze zastosowanie w technice. Filtry cząstek stałych mogą być wytwarzane z różnych materiałów, np. z kordierytu czy SiC. Idea zastosowania materiałów porowatych do budowy filtrów cząstek stałych jest obecnie uważana za rozwiązanie przyszłościowe, umożliwiające znaczne ograniczenie emisji PM. Wykorzystując właściwości materiałów porowatych można znacznie ograniczyć emisję PM w szerokim zakresie prędkości obrotowych i obciążeń silnika. Stosowane obecnie filtry cząstek stałych są zbudowane z wąskich kanałów, które podczas eksploatacji bardzo często ulegają zapychaniu. W artykule przedstawiono wyniki dotyczące badań struktury ceramicznej warstwy porowatej w zmiennych warunkach termicznych, co może prowadzić do pęknięć materiału ceramicznego oraz do zniszczenia warstwy katalitycznej Pd-Ru₃, naniesionej na porowatą strukturę Ti_4O_7 -SiC.

Introduction

Advance fuel technology in conjunction with an inherent high thermal efficiency have led to increased market share of diesel powered vehicles, especially in Europe, where the modern diesel passenger car is increasingly perceived by consumers as an environmentally friendly and cost-effective transport means. This increasing market penetration of the diesel powertrain is expected to continue, if the diesel engine is able to meet even more stringent emission limits in the future. The first successful market introduction of vehicles equipped with diesel particulate filters (DPF) and fuel borne catalyst assisted regeneration tool place in 2001 and since then DPFs have become possibly the most important and complex diesel emission control device (Fig. 1) [4].

The development of DPFs is also necessary to comply with heavy-duty engine emission standards while retrofit applications of passive DPF systems for heavy-duty

vehicles are already widespread during the last decade. The CRT particulate filter is a patented emission control technology that contains a platinum catalyst and a particulate filter. It is designed for use with large diesel engines, particularly large trucks and buses. The device is made up of two chambers. In the first chamber NO is oxidized to NO₂ by a platinum catalyst. The second chamber uses NO₂ to oxidize particulate material to CO₂. The catalyst also converts CO and HC into CO₂ and H₂O.

The CRT filter is capable of converting more than 90% of particulate materials, hydrocarbons and CO to water and CO₂. NO_x reductions are typically up to 10%. These improvements significantly reduce the tailpipe emissions from heavy vehicles. Over 35,000 CRT filters have been fitted on most major heavy duty diesel (HDD) engines in Europe, the US and Japan. It is the most widely used filter system for HDD engines and there are literally hundreds of



Fig. 1. Modern diesel particulate filter

1 – exhaust inlet, 2 – exhaust outlet, 3 – ceramic support, 4 – pressure sensor, 5 – fuel (reductant) injection [2, 9]

millions of miles of service and durability on CRT filters [9]. The Continuously Regenerating Trap (CRT) consists of a special catalyst followed by an exhaust filter capable of trapping soot and other particles generated by the combustion of diesel fuel. Specifically, the CRT works when:

1. Exhaust gases flow through the catalyst, which oxidizes carbon monoxide and hydrocarbons to carbon dioxide and water. At the same time, oxides of nitrogen in the exhaust stream, are partially converted to nitrogen dioxide.
2. The gases then pass through the filter, where the sooty particles are trapped.
3. Without being oxidized in some way, soot would build up and clog the filter.

Recent development (*Bardon et al., 2004; Boretto et al., 2004, Ogyu et al., 2004, Young et. al.*) in passenger car system are focusing on the so-called “fit-for-life” solution, eliminating the servicing of the DPF (ash removal) during the vehicle’s lifetime. Durability of the engine and emission control system is also very important in heavy duty vehicles [7].

Consequently, the emission control engineers must find practical and cost-effective solution, which in addition to particulate emission reduction should not hamper the also challenging task of reduction of nitrogen oxide (NO_x) emission (Fig. 2).

The price of the catalyst is one of the main barriers to the development of affordable fuel cells and automotive catalyst bed and DPF.

However, platinum is a very costly noble metal material, and alternatives are needed to reduce the cost for practical application of automotive catalysts and fuel cells (Fig. 3).

Optimization of the system is a very active DPF development area.

Palladium is a member of the platinum group of metals. It shares many of the chemical properties of platinum. Like platinum, it is used in catalytic converters for cars and for other catalysts that make use of its properties. In short, palladium is a highly useful and highly valued metal.

The role of the surface structure for the catalytic activity of a metal surface is studied using density functional theory. Monatomic steps at close packed Ru and Pd surfaces are identified to be highly reactive for the dissociation of diatomic molecules (NO, CO, N₂). The high reactivity is caused by the existence of a favorable reaction at which the complex reaction (e.g. stretched NO) coordinates to surface metal atoms [5, 6].

Recent theoretical work showed that the coverage of O on Ru (0001) is not limited to = 0.5 ML, which was for a long time

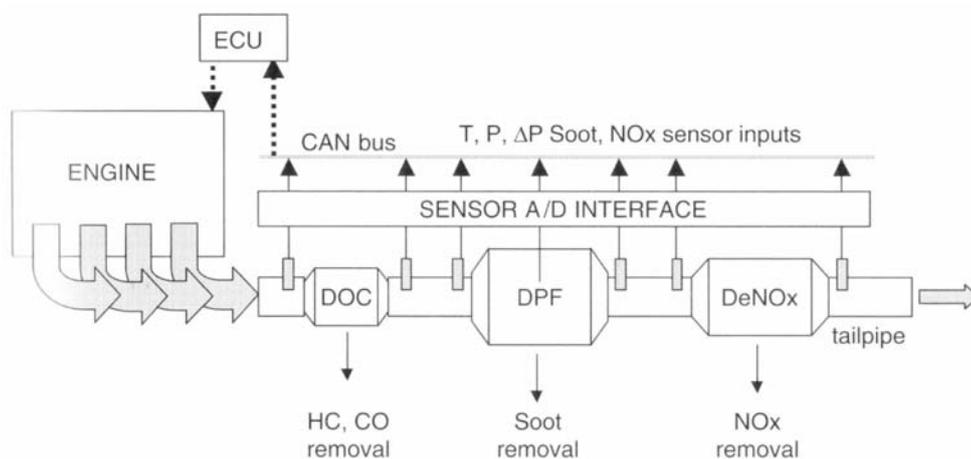


Fig. 2. An example of future integrated soot-NO_x emission control system. DPF stands for diesel particulate filter [10]

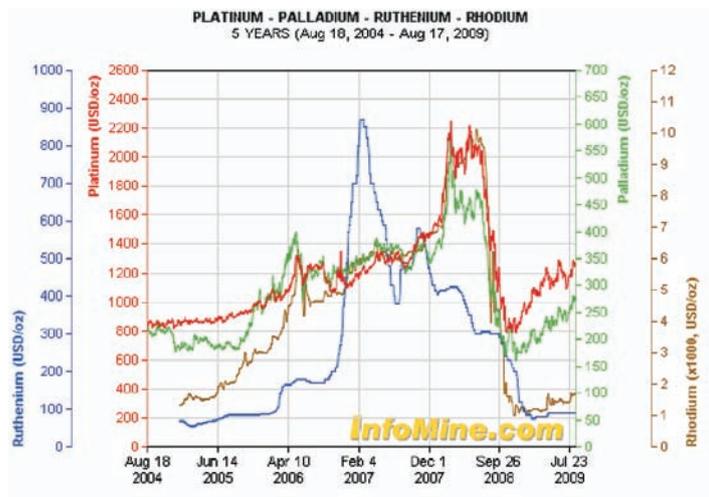


Fig. 3. Comparison between platinum, palladium, rhodium and ruthenium prices from 2004 to 2009 [3]

believed to be the saturation coverage under UHV conditions [8].

Subsequent experiments indicated an exceptionally high catalytic activity of the Ru (0001) surface (compared

to other Pd group transition metals), when high loads of O are stored not only on, but also inside the sample. In these experiments it was also observed that such surfaces are severely destabilized, leading to RuO₂ oxide formation and to RuO_x (x = 4) fragmentation at elevated temperatures [8]. We performed density functional theory calculations to gain an understanding of the nature of the O-Ru bonds and of the ensuing destabilization, when Ru is loaded with oxygen coverages between 0-2 ML. After a full O monolayer is completed on the surface, O starts to penetrate into Ru (0001), yet preferring to stay directly below the substrate layer and not deeper. We observe a tendency to form sub-surface islands, where the thus formed O-Ru-O surface is only loosely connected to the underlying substrate and may be considered as a precursor to oxide formation [1].

RuO₂ is one of the most widely applied oxide-catalyst materials owing to its high chemical stability, lower cost than Pt and good flexibility in fabrication. Such RuO₂ nanomaterials are especially attractive due to their tunable electronic and optoelectronic properties.

The Experiment

The Ti₄O₇ nanospheres are made by Flame Spray Pyrolysis-FSP process. The Ti₄O₇ sinters are obtained by PPS process at 970°C during 120 s.

Characterization

Reduction of titanium with hydrogen and water leads (during the FSP) to the formation of oxygen vacancies and Ti³⁺ ions, located on titanium surface and electrons that occupy donor sites in the bulk of titanium. The number of these defects is controlled by the equilibrium and is therefore quenched by the presence of water vapor.

High porosity – 67% composite filter material SiC-SiO₂-Ti₄O₇ has been produced during solid-state reaction between hollow parts- Ti₄O₇ and surface of SiC-Si
SiC → SiC + Si (atmosphere H₂; T = 380°C; t = 5 h),
SiC + Si + Ti₂O₃ → SiC + SiO₂ + Ti₄O₇ (atmosphere H₂; T = 1230°C; t = 1 h) (Fig. 4-6).

The vacuum impregnation method has been applied to synthesize the Magnelli phase-titanium oxide powder on high porosity supporting materials-substrate SiC-Si.

The composite consisting of SiC-Ti₄O₇ and pure SiC support (as reference material) were tested under two boxes – hot box temperature and cold box temperature for 800 cycles.

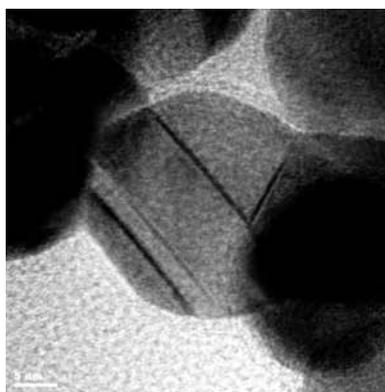


Fig. 4. HRTEM shows the crystal defects of flame generated Ti₄O₇ sphere

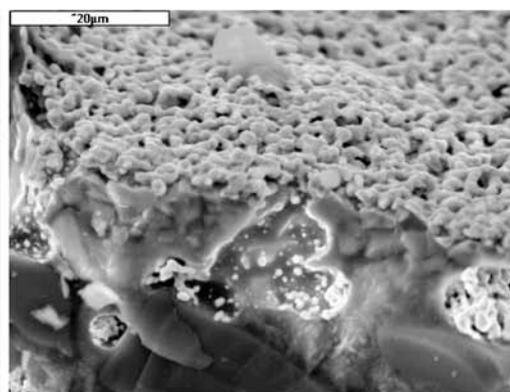


Fig 5. SEM image of Ti₄O₇ sphere bonded to SiC

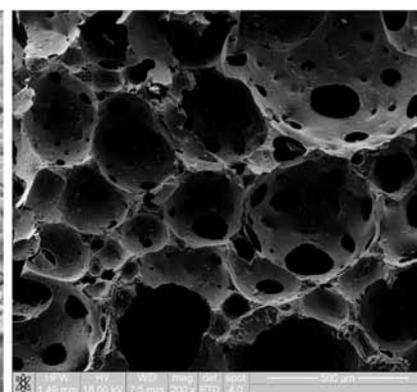


Fig. 6. SEM image of high porosity-macro- and mezo-pores Ti₄O₇ foam filter- ref.

A single basket product carrier moves between the hot and cold zones, subjecting the product to dramatic changes in temperature.

The samples to be tested are mounted inside an insulating enclosure open to the burner and air cooler side. The temperature at the front center, front edge and rear center of the probe was measured by three thermocouples (Fig. 7-9).



Fig. 7. Thermal shock test bench

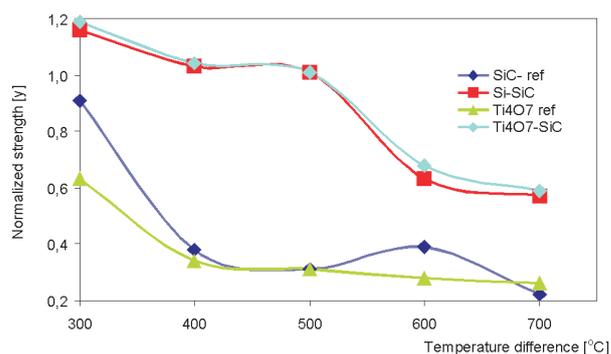


Fig. 8. Normalized fracture strength of DPF material after thermal shock loading

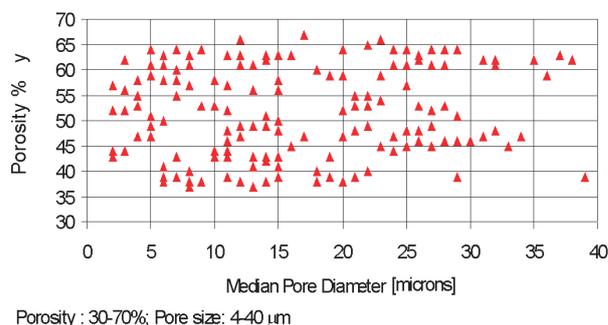


Fig. 9. Porosity and median pore size of Ti_4O_7-SiC

Conclusion

The final oxide bonded formulation – Ti_4O_7-SiC has similar thermal expansion to pure SiC grits and a higher elasticity deformation under load conditions than the reference. The higher elasticity performance could lead to higher resistance to thermal shock. Oxide bonded Ti_4O_7-SiC formulation has: similar thermal expansion, elasticity adjusted to adsorb thermal stress of monolith and prevent cracks from developing between the elements during repeated severe regeneration cycles.

It was shown that there is a significant improvement (by 1.5 times) in the thermal shock resistance of the layered

granular materials (at a lower value of porosity and higher strength) as compared to the materials having a granular structure. The results of our studies can be used for developing the materials for high-temperature installations.

In the catalyzed diesel particulate filter (CDPF), a catalyst is applied onto the filter media to promote chemical reactions between components of the gas phase and the soot (carbon) collected in the filter. It has been observed that catalytic combustion rate of combustible particulate matter on surfaces depends on the efficiency of the surface to make contact with particles.

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References

- [1] Height M.J., Mädler L., Krumeich F., Pratsinis S.E.: *Nanorods of ZnO made by flame spray pyrolysis*. Chem. Mater., 18, 572-578, 2006.
- [2] <http://en.wikipedia.org/wiki/File:7.8Isuzu7500.jpg>.
- [3] <http://www.infomine.com>.
- [4] Mädler L., Kammler H.K., Mueller R., Pratsinis S.E.: *Controlled synthesis of nanostructured particles by flame spray pyrolysis*. J. Aeros. Sci., 33, 369-389, 2002.
- [5] Mädler L., Stark W.J., Pratsinis S.E.: *Rapid synthesis of stable ZnO quantum dots*. J. Appl. Phys., 92, 6537-6540, 2002.
- [6] Mädler L.: *Liquid-fed aerosol reactors for one-step synthesis of nano-structured particles*. KONA, 22, 107-120, 2004.
- [7] Mueller R., Mädler L., Pratsinis S.E.: *Nanoparticle synthesis at high production rates by flame spray pyrolysis*. Chem. Eng. Sci., 58, 1969-1976, 2003.
- [8] Stamp C., Scheer M., Phys. Rev. B 54, 2868, 1996.
- [9] Tani T., Mädler L., Pratsinis S.E.: *Homogeneous ZnO nanoparticles by flame spray pyrolysis*. J. Nanopart. Res., 4, 337-343, 2002.
- [10] Wegner K., Stark W.J., Pratsinis S.E.: *Flame-nozzle synthesis of nanoparticles with closely controlled size, morphology and crystallinity*. Mater. Lett., 55, 318-321, 2002.