The effect of oxide nanospheres on strength fracture in DPF porosity sinters

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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.

1. Introduction

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 [1].

We investigated porous ceramic structure, under load condition – thermal shock, which can lead to fracture of ceramic material and damage the noble metal-catalyst-Pd-Ru_3, which is deposited on high porosity Ti_4O_7- SiC structure.

2. The Experiment

The Ti_4O_7 nanospheres are made by Flame Spray Pyrolysis-FSP process. The Ti_4O_7 sinters are obtained by PPS process at 970°C during 120 s.

3. Characterization

Reduction of titanium with hydrogen and water leads (during the FSP) to the formation of oxygen vacancies and Ti^{3+} 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- SiO_2-Ti_4O_7 has been produced during solid-state reaction between hollow parts- Ti_4O_7 and surface of SiC- Si.

$SiC \rightarrow SiC+Si$ (atmosphere H_2; T= 380°C; t=5 h)

$SiC+Si + Ti_2O_3 \rightarrow SiC+SiO_2 + Ti_4O_7$ (atmosphere H_2; T= 1230°C; t=1 h)

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-Ti_4O_7 and pure SiC support (as reference material) were tested under two boxes- hot box temperature and cold box temperature for 800 cycles.

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

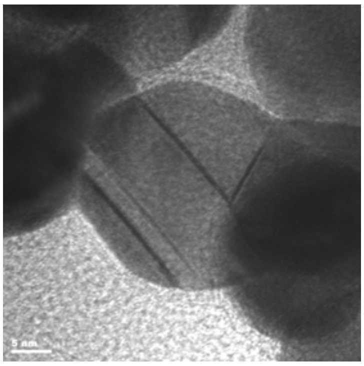

Figure 1. HRTEM shows the crystal defects of flame generated Ti_4O_7 sphere.

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.

Figure 2. Thermal shock test bench.

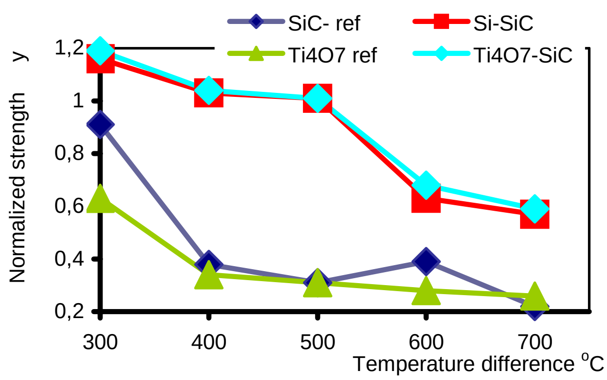

Figure 3. Normalized fracture strength of DPF material after thermal shock loading.

4. 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.

[1] Patent claim J. Merkisz, P. Fuć, D. Obłąkowska.

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Abstract

High porosity ceramics and ceramic-metal composites are now widely applied to a number of fields i.e. in diesel particular filter-DPF. The DPF may be manufactured from different materials i.e. cordierite, silicon carbide. 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 porosity Ti_4O_7. There was investigated the response of thin, porous ceramic walls which are in the thermal shock and vibration mode, during exploitation, which can lead to fracture of ceramic material and destroy the noble metal-catalyst-Pd-Ru_3, which is deposited on high porosity SiC. Porous SiC ceramics has been used in many practical applications because of its many excellent properties, such as excellent thermal and mechanical properties and high thermal shock resistance. In addition, porous SiC has good permeability to gases and liquids, so that the materials have been considered one of the most promising candidates for hot-gas filtration i.e. in DPF. The Ti_4O_7 nanospheres are made by Flame Spray Pyrolysis-FSP process. The FSP process was lead by using an external-mixing gas assisted atomizer supported by premixed hydrogen and oxygen flamelets. Liquid precursor such as Titanium IV isopropoxide in an alcohol solvent was used as precursor Ti_4O_7. Combustion of liquid precursor droplets is used to obtain high purity and relative narrow size nanoparticles of Ti_4O_7. Composite consisting of SiC-Ti_4O_7 and pure SiC support (as reference material) were tested under two boxes- hot box temperature and cold box temperature during 800 cycles. Nanoparticles of Ti_4O_7 were investigated by BET surface area analysis and measured by the Z-sizer. Composite consisting of SiC-Ti_4O_7 was examined by SEM, TEM techniques.

1. Introduction

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. Figure 1 shows SEM image of PM- high temperature.

The present commercial DPF-SiC with excellent filtration efficiency is composed of many elements mainly to avoid thermal shock failure during severe regeneration. The pore size and porosity of such a material are also too small to serve as a catalyst support for the impregnated catalyst in the near future. In fact the DPF-SiC body has a 91% SiC grit content bonded with a proprietary inorganic composition based on refractory oxides chosen for their elasticity, resistance to chemical attack and with thermal expansion characteristics similar to the SiC grit. The second target was to have a minimum number of elements to build the final DPF product.

The following physical properties and geometry were optimized and compared with DPF--SiC commercial reference: coefficient of thermal expansion, thermal conductivity, porosity, pore size distribution, permeability, pressure drop, thermal shock resistance, and number of elements required to assemble the composite DPF and cell wall thickness.

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 the noble metal-catalyst-Pd-Ru_3, which is deposited on high porosity Ti_4O_7- SiC structure.

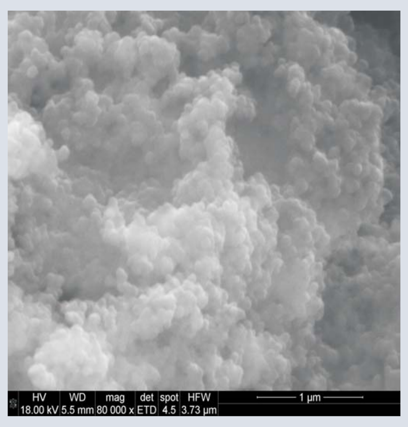

Figure 1. SEM image of PM- high temperature.

2. Experiment

The Ti_4O_7 nanospheres are made by Flame Spray Pyrolysis-FSP process. The FSP process was performed with the use of an external- mixing gas assisted atomizer supported by premixed hydrogen and oxygen flamelets. Liquid precursor such as Titanium IV isopropoxide in an alcohol solvent was used as a precursor for Ti_4O_7. A combustion of liquid precursor droplets is used to obtain high purity and relative narrow sized nanoparticles of Ti_4O_7. Pulsed Plasma Sintering-PPS is an effective method of sintering of ceramic materials. The Ti_4O_7 sinters are obtained by PPS process at 970 °C during 120 s. Figure 2 shows the image of high porosity -Ti_4O_7 foam filter- ref.

The electronic conductivity of titanium based ceramics originates from the presence of Ti^{3+} ions. There are two ways to create of Ti^{3+} ions in the TiO_2 structure: by creating oxygen vacancies and shear planes (usually by heating TiO_2 in a reducing atmosphere) or by introducing appropriate donor dopants to create crystal defects. Reduction of titanium with hydrogen and water leads (during the FSP) to the formation of oxygen vacancies and Ti^{3+} 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. Figure 3 shows the crystal defects of flame made Ti_4O_7 sphere.

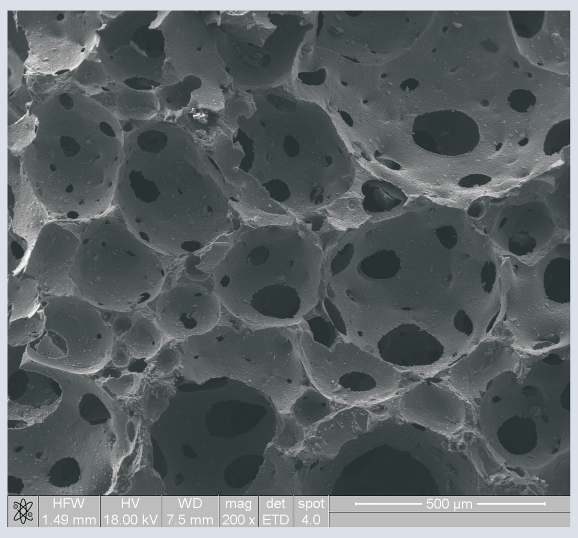

Figure 2. SEM image of high porosity- macro- and mezo-pores Ti_4O_7 foam filter- ref.

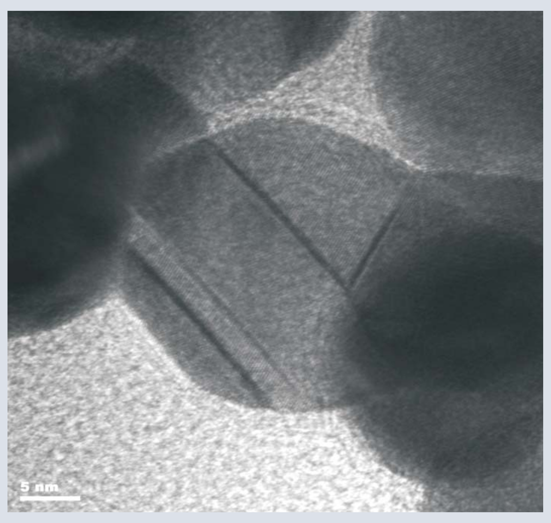

Figure 3. HRTEM shows the crystal defects of flame generated Ti_4O_7 sphere.

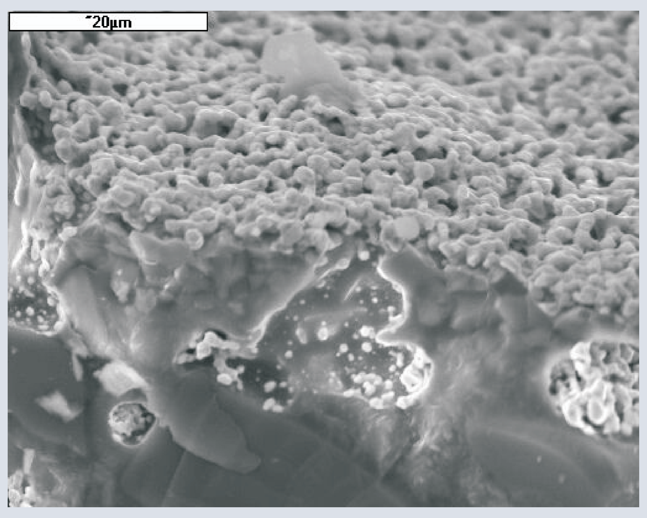

Figure 4. SEM image of Ti_4O_7 sphere bonded to SiC.

High porosity 67% composite filter material SiC-SiO_2-Ti_4O_7 has been produced during solid-state reaction between hollow parts- Ti_4O_7 and surface of SiC-Si. SiC SiC+Si (atmosphere H_2; T= 380 °C; t=5 h) SiC+Si + Ti_2O_3 SiC+SiO_2 + Ti_4O_7 (atmosphere H_2; T= 1230°C; t=1 h). The vacuum impregnation method has been applied to synthesize the Magnelli phase-titanium oxide powder on high porosity supporting materials- substrate SiC-Si. Figure 4 presents the image of Ti_4O_7 sphere bonded to SiC.

The porosity of Ti_4O_7, the pore size- macropore in size of 1500 nm, exhibits an open-cell structure with interconnected micropores which provide the potential for the transport of the gases by the filter body. Figure 6 presents the image of porosity $PdRu_3$-sinter. Figure 5 TEM presents a micro-section of Ti_4O_7 nanosphere.

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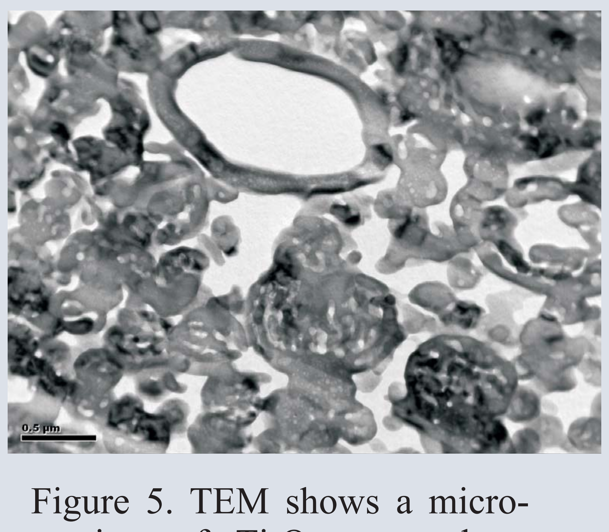


Figure 5. TEM shows a micro-section of Ti_4O_7 nanosphere sinters by PPS method.

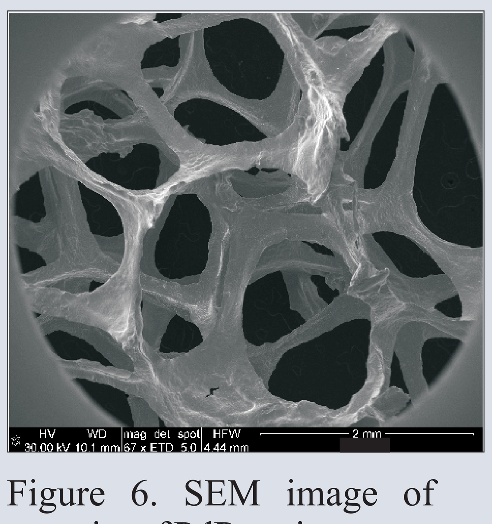


Figure 6. SEM image of porosity of $PdRu_3$-sinter.

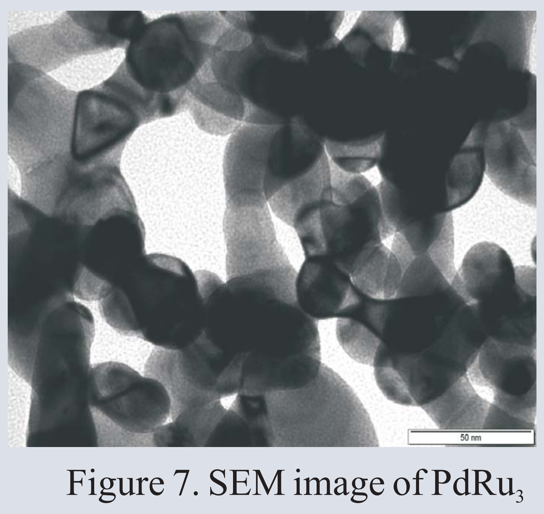


Figure 7. SEM image of $PdRu_3$ deposited on high porosity Ti_4O_7- SiC.

The $PdRu_3$ system is an active part of the second generation catalyst support of DPF. 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 the response of thin, porous ceramic walls which are in the thermal shock and vibration mode, during operation, which can lead to a fracture of ceramic material and damage the noble metal-catalyst, which is deposited on high porosity SiC. We investigated porous ceramic structure, under load conditions thermal shock, which can lead to a fracture of the ceramic material and damage the noble metal-catalyst-Pd-Ru_3, which is deposited on high porosity Ti_4O_7-SiC structure. Figure 7 shows the image of $PdRu_3$ catalyst, deposited on high porosity Ti_4O_7-SiC.

3. Results and discussion

Wall-flow DPFs and ceramic catalyst supports generally comprise thin-walled ceramic honeycomb structures with high geometric surfaces areas and, in some cases, with extensive interconnected porosity for good fluid filtration. Ceramic filters, in particular, must exhibit high mechanical strength for handling and superior thermal shock resistance in operation. The thermal shock resistance (TSR) of a composite ceramic body is related to the stress at fracture (as given by strength at fracture or Modulus of Rupture- MOR), the elastic modulus (E) and the strain at fracture i.e. the product of thermal expansion coefficient (α) and thermal gradient (ΔT), through the following expression:

TSR oc- MOR

E » α » ΔT

High levels of thermal shock resistance have typically been sought by attempting to obtain extremely low values of thermal expansion coefficient, or through methods to reduce thermal gradients in high temperatures. However, it can be seen from the expression above that the use of a material with a sufficiently high strength and a sufficiently low bulk elastic modulus (i.e. an increased strain tolerance) could offer adequate thermal shock resistance for some applications.

There are several critical issues that the DPF confronts. One is the prevention of breakage due to the thermal loading during regeneration process. Therefore, it is desirable for the DPF materials to have a high thermal resistance and a thermal stress capability.

The coefficient of thermal shock resistance R is generally represented by the following equation.

$$R = \sigma / (E * \alpha * (1-\mu))$$

σ - strength
E - elastic modulus
α - thermal expansion coefficient
μ - Poisson's ratio

The implementation of the Ti_4O_7 sphere into SiC ceramic effectively works to lower the elastic modulus of DPF, which is leading to the higher thermal shock resistance.

We investigated the response of thin, porous ceramic walls which are in the thermal shock and vibration mode, during operation, which can lead to a fracture of ceramic material and damage of the noble metal-catalyst-Pd-Ru_3 which is deposited on high porosity SiC. The composite consisting of SiC-Ti_4O_7 and pure SiC support (as reference material) were tested under two boxes- hot box temperature and cold box temperature for 800 cycles. 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.

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.

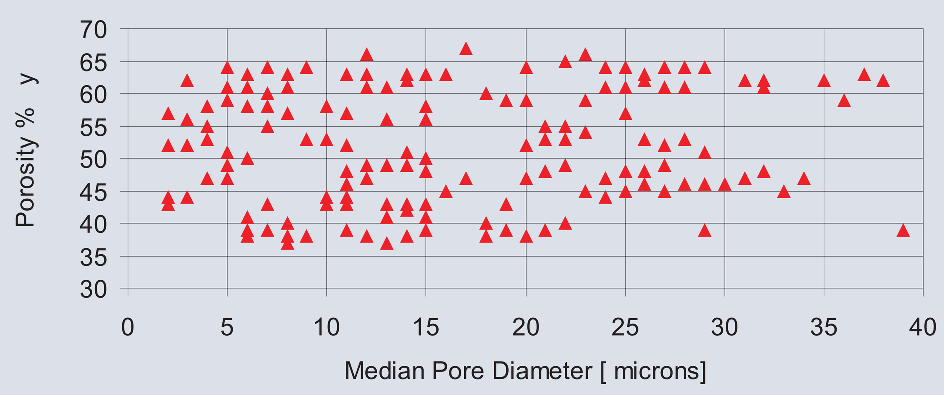
The following thermal shock test conditions were used to perform this test. The temperature of the probes was increased from 25 °C to 800 °C. The elements were cycled 800 times in an automated manner in the atmosphere of natural gas burner- hot box and a 5 bar air pressure- cold box. Mechanical strength, elasticity modulus and porosity were measured before and after the thermal shock testing. After 800 cycles no cracking was observed. The Table 1 summarizes the typical properties of materials- SiC-ref.; Ti_4O_7-ref and recrystalized, tested materials- Si-SiC, Ti_4O_7-SiC.

Figure 8. Thermal shock test bench.

Table 1. Characteristic of DPF materials.

Material / Properties	SiC-ref	Si-SiC	Ti_4O_7-ref	Ti_4O_7-SiC
Porosity [%]	45	47	40	43
Mean pore diameter [μm]	10	18	13	16
Thermal expansion 25-800 °C [ppm/°C]	4,8	4,1	8,1	4,9
Fracture strength [MPa]	56	29	32	43
Elastic modulus [GPa]	48	22	12	21

Figure 9 presents fracture strength of DPF materials, after thermal shock loading. As can be seen, the reference materials decrease the strength at the temperature difference of 300-500°C-SiC ref. and Ti_4O_7-ref. On the other hand, the materials such as Si-SiC and Ti_4O_7-SiC are very stable from 300°C to 500°C, that indicating higher thermal shock resistance of those materials. In order to obtain high porosity ceramics with a required mechanical strength, the bonding strength at the interface between Si-SiC and Ti_4O_7-SiC particles turns out to be an important factor. Here, the reference materials SiC ref. and Ti_4O_7-ref show low mechanical strength due to the narrow bonding area. On the other hand, the materials such as Si-SiC and Ti_4O_7-SiC show high mechanical strength due to the forming of new phases at the interfaces.



Porosity : 30-70%; Pore size: 4-40 μm

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

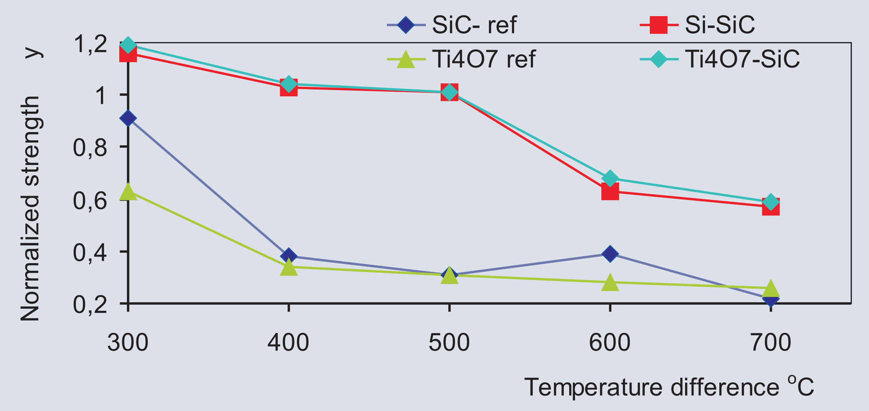


Figure 10. Normalized fracture strength of DPF material after thermal shock loading.

According to the embodiments of the invention, the composite ceramic body comprises a substantially non-microcracked first ceramic phase with relatively good thermal shock resistance, and a minor second phase of a material that imparts at least a reduction in the elastic modulus of the composite ceramic in the temperature range of 600°C-1100°C, as compared with the room temperature value of the elastic modulus of the composite ceramic and wherein a total porosity (% P) of the body is % P > 45%.

4. 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.

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The porous Ti_4O_7- SiC has good permeability to gases and liquids, so the materials have been considered one of the most promising candidates for hot-gas filtration i.e. in DPF.