Next Generation Nanospring-enhanced Catalytic Converters

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ABSTRACT

Air pollution generated from automobile emissions is an area of general concern because of the environmental impact associated with such emissions and the growth in the world vehicle fleet. Significant developments in automotive catalytic converters has occurred with three-way catalysts (TWC). However, major challenges remain, particularly because of regulatory demands for better and better performance. The approach proposed here is to engineer the cell walls of a catalytic converter monolith using NanospringTM technology. The Nanosprings are bonded directly to the cordierite surface without the use of binders and can be coated with a wide range of metal oxides and metal nanoparticles. Due to the use of Nanosprings a significantly higher fraction of the metal nanoparticle surface is accessible to exhaust gases, thus deceasing the overall amount of precious metal required.

Keywords: Silica Nanosprings, nanomaterials, catalytic converters, cordierite

1 INTRODUCTION

Pollution from automobile emissions is an area of general concern because of the environmental impact associated with such emissions and the growth in the world vehicle fleet [1]. Catalytic converters had widespread roll out in the US market starting in 1975 by the Engelhard corporation. Since then they have become the standard in exhaust pollution control. Significant developments in automotive catalytic converters has occurred with three-way catalysts (TWC) representing probably the most important of these developments [2]. Their efficiency at reducing carbon monoxide, NO_x , and unburned hydrocarbons resulted in a dramatic reduction in air pollution even as more cars were added to the road [3]. However, major challenges remain, particularly because of regulatory demands for increased performance. Next generation catalytic converters must possess the following properties [4]:

• High activity and selectivity

- Very fast light-off (<20s)
- High thermal stability
- High oxygen storage capacity

An additional desirable goal is to reduce the platinum group metal (PGM) content in order to lower costs. The majority of research has been in engineering the catalyst and the wash-coating process of applying them to catalytic converter insert materials to achieve these goals. Significantly less research has gone into making more efficient use of the precious metal and increasing catalytic converter performance by means of engineering the substrate.

A recent approach towards increasing the surface area of the underlying substrate was developed by Dow Chemical Corporation to be used as a diesel particulate filter (DPF) insert [5], [6]. This material consists of micron-sized mullite protrusions that project out into the gas stream to capture and burn diesel particulates [5]. Particulate filters are an integral part of any pollution control system for diesel applications. The new regulations from Europe, Japan and the United States demand a reduction of particulate matter (PM) in both quantity and size. Therefore, the importance of finding a highly efficient filter that does not compromise performance and fuel mileage becomes increasingly important. In addition, it is also desirable that these particulate filters reduce NO_x and CO emissions.

This work presents an alternative approach for next generation catalytic converters by coating current ceramic inserts with high surface area silica Nanosprings. The Nanospring material is chemically bonded to the ceramic substrate without employing binders. The presence of Nanosprings has a negligible effect on the exhaust back pressure, due to the size and open porosity of the Nanospring mats. PGM and metal oxides can be deposited directly on the Nanosprings increasing significantly the surface area that will be accessible to exhaust gases, thus deceasing the overall amount of precious metal required.

An important aspect of catalytic converter technology is lifetime. Metal nanoparticles form on the surface of silica Nanosprings exhibit significally lower tendencies for ripening than when form on other ceramic surfaces. For example, gold nanoparticles on silica Nanosprings are stable at temperature above termodinamic melting point of the particles [7].

2 TECHNICAL DESCRIPTION

To fabricate the catalytic converter inserts cordierite monoliths with a cell count of 400 cpi and a wall thickness of 6 mil, as shown in Figure 1a, were cleaned with deionized water to remove any residual particles and then dried at 200°C for 30 minutes. The technology used to grow the Nanosprings has been previously reported by Wang et al. [8] and McIlroy et al. [9]. Due to the pending aplication for a US patent [10] on Nanospring technology, only a condensed description of the process will be presented. The Nanospring synthesis was performed in a furnace operated at atmospheric pressure. The general principles of this furnace were discussed in detail by McIlroy *et al.* [9]. The process uses a thin gold layer as a catalyst, which is then exposed to a proprietary silicon precursor. During the Nanospring synthesis, a constant oxygen (O_2) flow rate is maintained concomitant with the silicon precursor. With a growth time of 15 minutes, a $120\mu m$ thick Nanospring mat coating the cordierite cell walls was achieved, shown in Figure 1b.

Figure 2a shows an scanning electron microscope (SEM) image of an internal cross section of a cordierite monolith coated with Nanosprings. Figure 2b shows a higher magnification of an internal cordierite wall coated with Nanosprings. These images show the coating thickness and uniformity across the whole length of the cordierite substrate. The internal thickness of the mat was measured to be approximately 100μ m.

Figure 3 shows a much thinner Nanospring layer on a cordierite monolith wall. The thickness of the mat is controllable by the growth parameters given by Wang *et al.* [8] and can adapted to match different requirements. For the present work 3 different mat thickness were fabricated: a thick mat approximately 120μ m, a medium thickness mat approximately 60μ m and thin mat approximately 15μ m.

The Nanosprings synthesized on the ceramic monoliths were then coated with palladium (Pd) nanoparticles employing the same atmospheric CVD technique used to deposit the Nanospring catalyst. The Pdprecursor was prepared from a palladium (II) nitrate purchased from Strem Chemicals. The Pd reduction was performed at 500°C for 30 minutes with a constant nitrogen (N_2) and hydrogen (H_2) flow.

Gold nanoparticle coated samples were prepared by depositing Au nanoparticles on the surface of silica Nanosprings by plasma enhanced chemical vapor deposition (PECVD). Samples were then heated to temper-



Figure 1: a) Cordierite catalytic converter monolith, b) SEM image of a cordierite monolith conformally coated with Nanosprings.



Figure 2: a) SEM cross section image of Nanospring coated cordierite b) SEM image of the Nanospring coated cordierite wall.

ature up to 600° C for 24 hours in air. Samples were imaged and a particle size distribution was determined



Figure 3: SEM image of a thinner Nanospring mat on a cordierite monolith wall.

before and after heating as shown in Figures 4a and 4b, typically a minimum of 400 particles were counted. The average nanoparticle size of was determined to be \approx 3nm before and after heat treatment.

Nanosprings themselves are stable up to 1025°C.



Figure 4: Au nanoparticles on silica Nanosprings a) before heat treatment (average size \approx 3nm), b) after heat treatment (average size \approx 3nm).



Figure 5: Silica Nanosprings after heat treatment at 1050°C in air for 24 hours.

Samples were treated for 24 hours in air and under steam flow and imaged before and after to check for nanostructural changes to the springs. Figure 5 shows a SEM image of a Nanospring mat after heat treatment. No structural changes were obsverved in the silica Nanosprings after heat treatment.

Back pressure measurements were carried out for 3 different thicknesses of Nanosprings coated on cordierite. Five samples of each thickness were run on a test bench at varying space velocities and the corresponding pressure drop was measured. The data are plotted in Figure 6.



Figure 6: Backpressure measurements comparing Nanospring coated cores at 3 separate thickness against bare cordierite.

As would be expected mat thickness is directly proportional to the pressure drop. For a thin coating of Nanosprings run at a space velocity of $250 \ Khr^{-1}$ there is a back pressure increase of approximately 25% or

 3.39×10^{-4} bar (0.01 inHg) compared to bare cordierite. The pressure goes up to about 38% or 5.08×10^{-4} bar (0.015 inHg) for a medium mat, and 115% or 1.19×10^{-3} bar (0.035 in Hg) increase for the thickest mats.

3 CONCLUSIONS

Catalytic converters based on Nanospring technology should demonstrate superior performance and lifetime increase compared to existing wash-coat technology currently on the market. Nanosprings exhibit high temperatue stability beyond that normally encounter in catalytic converter applications. Furthermore, the Nanosprings surface reduces the tendency for ripening of supported precious metals nanoparticles.

Nanospring coated cordierite should be an excellent base material for next generation catalytic converters due to the increase in surface area and concomitant exhaust gas exposure.

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