CASE NOTE

How Niobium Technology Can Increase the Efficiency of Catalytic Converters

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The primary purpose of this document is to highlight an area of cutting-edge research where niobium technology has the potential to increase the efficiency of catalytic converters in gasoline vehicles.

Catalytic converters were first introduced by the automotive industry in the 1970's to address deteriorating air quality and their development has been evolving ever since. This area of technology is becoming increasingly important as the number of vehicles on the road continues to grow on a global scale (Figure 1).

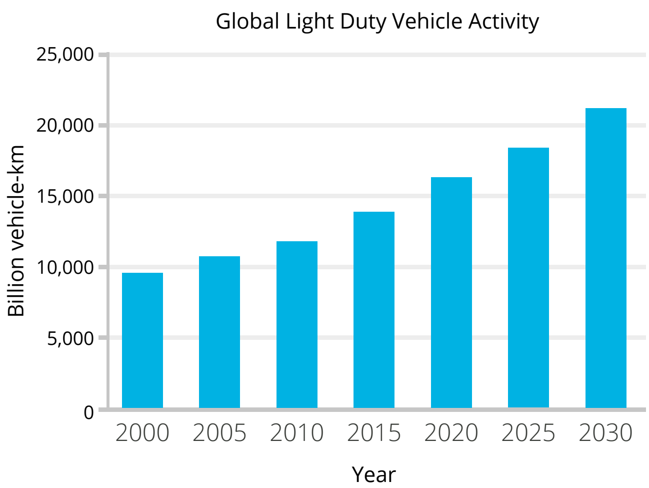

Figure 1. Annual global vehicle activity [1].

Furthermore, governments are implementing strict legislation relating to emission targets which are driving technology developments in the automotive sector.

Catalytic converters, therefore, will play an instrumental role in meeting increasingly stringent legislative requirements, through their role in converting toxic emissions into harmless end products. Their widespread introduction has already had an impact, despite increasing vehicle numbers, by improving air quality in urban areas in particular.

Three Way Catalytic Converters

First introduced commercially in 1980, Three Way Catalytic Converters (TWCs) are now available in most gasoline based passenger vehicles. They simultaneously carry out three oxidation and reduction reactions, as shown below in the car's exhaust system, typically converting around 98% of nitrogen oxides, carbon monoxides and hydrocarbons from the engine.

Reduction of nitrogen oxides to nitrogen and oxygen:

$$H_2 + NO \rightarrow N_2 + H_2O$$

Oxidation of carbon monoxide to carbon dioxide:

$$CO + H_2O \rightarrow H_2 + CO_2$$

Oxidation of unburnt hydrocarbons (HC) to carbon dioxide and water:

$$C_xH_{2x+2} + [(3x+1)/2]O_2 \rightarrow xCO_2 + (x+1)H_2O$$

TWCs contain combinations of precious metals, dispersed on high surface area carriers coated onto the walls of a ceramic honeycomb monolithic structure (Figure 2).

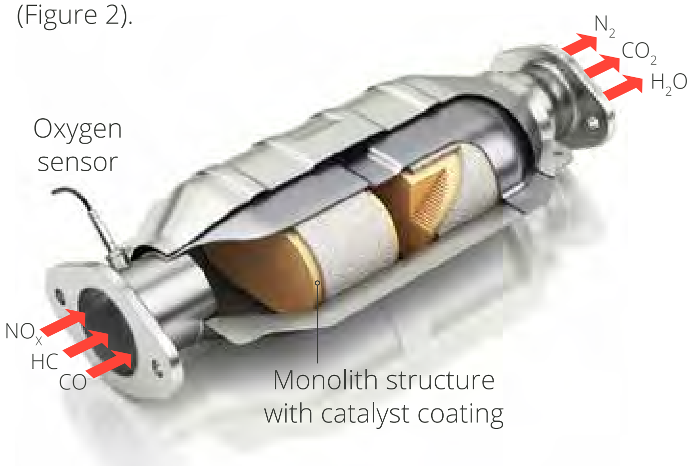

Figure 2. Three Way Catalytic Converter.

The precious metals, palladium and rhodium, act as the active catalysts for the reduction and oxidation reactions. Other components support the reactions by providing a high surface area (alumina) and as oxygen storage promoters (CeO_2-ZrO_2 mixed oxides), which enhances the catalytic activity of the precious metals.

Although the oxidation and reduction reactions within the TWC are straightforward, the biggest challenge to this technology is optimizing the operating conditions. TWCs only work efficiently within an optimum operating temperature range and with an accurately adjusted residual oxygen content in the exhaust gas.

Oxygen Storage Component

Oxygen levels are influenced by the ratio of air to fuel in the exhaust gas, which fluctuates as driving conditions change (eg during acceleration). The amount of free oxygen therefore has an influence on efficiency of the reduction and oxidation reactions taking place. If there is too much free oxygen, caused by a lean air to fuel mixture, then the reduction efficiency is low. Conversely, the oxidation efficiency is reduced when a rich air to fuel mixture results in a low availability of free oxygen.

To summarize, the reduction of NO_x is inefficient when oxygen contents are too high and HC / CO oxidation is inefficient when oxygen contents are too low. Maintaining a balanced availability of oxygen is therefore critical to the performance of the TWC.

This continuous balancing requires a closed loop engine control system, to ensure the air to fuel ratio is within a narrow operating band, and through the oxygen storage component (OSC). The OSC plays an important role in buffering the amount of available oxygen during the time taken for the air to fuel ratio to be adjusted via the closed loop system [2].

The most widely used OSCs are ceria-zirconia (CeO_2-ZrO_2) solid solutions, with ceria, CeO_2 being the active component. Cerium attracts oxygen and under high oxygen conditions, absorbs oxygen to allow the reduction of NO_x. Under low oxygen conditions, it releases stored oxygen, enabling the efficient oxidation of HCs and CO. This allows the active precious metal catalysts to operate efficiently under slightly fuel rich and slightly fuel lean conditions for very short periods of time.

Where can niobium bring potential benefits?

The OSC function of CeO_2 in TWC efficiency is well established [3] and in the mid 1990's, pure CeO_2 was gradually replaced by CeO_2-ZrO_2 mixed oxides as OSC materials, due to their higher thermal stability [4]. This was to meet the demands of higher operating temperatures in the exhausts of more modern vehicles and represented a milestone in the development of TWC technology. As the technology developed even further, additional elements were being considered by the industry and Delphi Catalysts Inc. (now Umicore Automotive Catalysts USA), were granted a patent in 2003 which claimed that niobium oxides can be used as a promoter to improve the OSC of TWCs [5].

The opportunity for niobium, which has high redox activity when incorporated into solid solutions, was originally driven by the desire to reduce reliance on rare earth oxides due to concerns over supply and price. The patent and subsequent research [6,7] confirmed that adding niobium to ZrO_2-CeO_2-Y_2O_3 solid solutions did increase the oxygen storage capacity.

The original patent identified a potential new niche application for niobium and prompted further research which was carried out at Columbia University (New York, NY USA) and CBMM (Araxá, MG Brazil). The aim of the research was to substantiate and elaborate on the current state of the art to produce supplementary, and more fundamental data to understand more about the optimum performance of niobium in enhancing OSC.

This research identified the optimum niobium content of 7.5 cat mol% in the formulations studied (Figure 3) [6]. This level led to significantly higher oxygen storage capacity than the baseline niobium-free sample at temperatures within the normal operating range of the TWC. In addition, during redox cycling tests performed at 500 °C, the niobium containing material also had higher rates and extents of reduction and oxidation than the niobium-free baseline material.

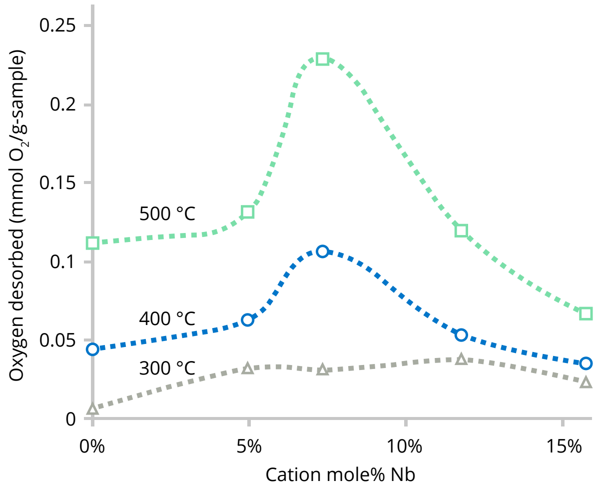

Figure 3. Niobium optimum amount (8 wt.%) on increasing OSC material performance at 500 °C [6].

Following the publication of these promising results, research work is on-going and will no doubt make a substantial contribution to the validation and take up of this technology by the automotive industry world-wide.

> Niobium technology has the potential to play a substantial role in the advancement of TWC technology, helping the industry to meet the requirement for cleaner and greener vehicles. Further reducing emissions will not only have a profound impact on the environment, but also on our quality of life. The research community must keep developing new materials and technologies which further reduce our impact on the environment through the smarter use of natural resources.

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