ISSN: 1231-4005
e-ISSN: 23540133
DOI: 10.5604/01.3001.0010.3053

THE POSSIBILITIES AND DEVELOPMENT OF IN-CYLINDER CATALYTIC COATING

Monika Andrych-Zalewska

Wroclaw University of Science and Technology
Department Vehicle Engineering
Wybrzeże Wyspiańskiego Street 27, 50-370 Wroclaw
tel.: +48713477918
e-mail: monika.andrych@pwr.edu.pl

Abstract

Due to the legal changes in the exhaust emission limits in the European Union meeting the new norms becomes more challenging for car manufacturers. The recent progress in the exhaust aftertreatment technology and commercially available aftertreatment systems. However, as the exhaust, systems become more and more complex the problem of high emissions in many engine-operating points that are not currently a part of the type approval tests remains. The article aims to address the limitations of the oxidation catalysts in current aftertreatment systems, mainly their light-off temperature, by investigating new options for in-cylinder catalysts. Placing the catalytic layer within the combustion chamber avoids a number of problems associated with these catalysts being a part of the aftertreatment system. Engine emission tests have been performed comparing the effects of using an in-cylinder Pt-Rh catalytic layer in relation to hydrocarbon and nitrogen oxides emissions. The viable methods of producing a catalytic layer on engine components along with the choice of components to use for catalytic surfaces have also been discussed.

Keywords: *combustion engine, in-cylinder catalyst, exhaust emissions*

1. Introduction

The problem of harmful emission components lies at the basis of current motorization development and legislative action aimed at reducing the air pollution caused by road transport. The regularly tightened limits for harmful emission components imposed on motor vehicle manufacturers force the application of new methods to reduce the amount of pollutants in the exhaust gases. The solutions observed in the last dozen or so years, that allow meeting the type approval tests requirements, are mainly related to advanced exhaust aftertreatment systems – the use of catalytic converters, particle filters and selective catalytic reduction technology. All of these technical solutions concern the treatment of the exhaust gases that have already left the internal combustion engine, and they do not contribute to limiting the formation of harmful compounds in the combustion process. From the point of view of internal combustion engines ecological properties, solutions that would limit the formation of harmful compounds in the combustion chamber are highly desirable, e.g. by shortening the ignition delay time. One of the available technical solutions to reduce the amount of impurities present in the combustion chamber is the catalytic coatings implanted on the engine components – the glow plug, cylinder head or piston crown [2]. The proposed solution of an in-cylinder catalyst would aim to tackle the problem of harmful compounds emission at their very source of origin, thus taking advantage of the most pivotal point in their formation. Additionally placing the catalyst within the engine cylinder allows for achieving the catalyst light-off temperature much earlier than it is the case for catalytic aftertreatment systems placed in the exhaust. Most of the aftertreatment systems used in modern day combustion engine vehicles rely on the heat of the flue gas to achieve operational temperature, and many of those systems operate at a considerably lower efficiency during engine cold start, and during short engine operating times. Hence, the optimal location for a catalyst is as close to the combustion process as possible. This thinking led to the concept of in-cylinder catalytic surfaces as an efficient solution to the problem of engine exhaust emissions reduction.

The ability of an in-cylinder catalyst to reach high efficiencies during cold engine start is one of the key features of this solution. This results from the ever-changing exhaust emission limits, both in the EU and worldwide. The emission limits stated by the current emission regulations constitute an approximately 99% reduction in limit values when compared to the initial limits from 25 years ago (Fig. 1). Such a significant change over the span of less than three decades puts significant pressure on engine manufacturers to design and produce engines and aftertreatment systems capable of meeting these new norms. However, the change in numerical limits is only one of the aspects that challenge car manufacturers. It is important to note the impact of the type approval of test cycles, which also change over the years. Up until now type, approval tests were performed mostly on engine dynamometers, or chassis dynamometers. It has been shown time and time again that emission tests in such simulated conditions do not accurately represent the actual driving emissions [7]. The current type approval tests for passenger cars do not consider many non-ideal engine conditions (such as a cold start, or worn engine) or various road conditions (such as elevation, weather conditions or traffic). New and improved testing procedures are being steadily phased in; however, leading to the introduction of Real Driving Emissions testing (RDE) using Portable Emission Measurement Systems (PEMS) to more accurately determine vehicle emissions in real driving conditions. These new tests will steadily expand the range of operating points in which the engine will be expected to perform within the legal emission limits. This includes cold engine start conditions, which have thus far been mostly ignored by the manufacturers.

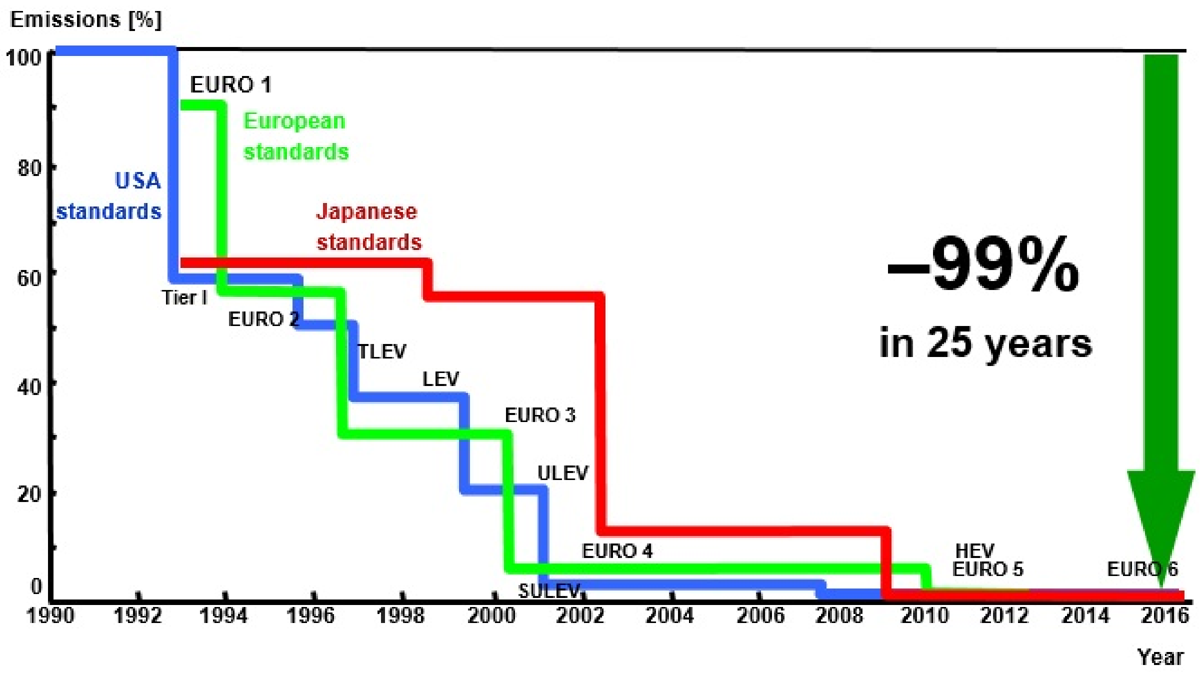

Fig. 1. Changes in overall emission limits as a percentage of the original USA standards from 1990

2. Methodology of catalytic surfaces coating

One of the most important properties of catalytic surfaces is the service life, which depends mostly on their application technique [1, 5]. One of the most popular and easiest methods is the plasma spray method, which dates back to the fifties of the twentieth century. Plasma spraying is usually carried out under ambient conditions – APS (Atmospheric Plasma Spraying). Depending on the type of sprayed elements or chemical compounds, the conditions for the formation of the catalytic layer may vary [6].

Plasma spray coatings typically consist of high melting point materials such as metal oxides and carbides, as well as pure metals, metal alloys and mixtures:

- ceramic coatings – aluminum oxide, chromium oxide, and zirconium oxide coatings,
- cermet coatings – mixtures of ceramic and metal materials with different chemical and phase compositions,
- metal coatings – tungsten and molybdenum coatings, as well as alloy coatings of cobalt, chromium or nickel etc. [6].

From the perspective of the catalytic coating life, ion implantation is a superior solution to plasma spraying, indicated as a solution with high future potential [3]. The use of this method, however, involves a greater financial cost. Ionic implantation is mainly used to improve the usable properties of implanted materials. The material-based process itself is based on the use of high dopants kinetic energy. Dopant atoms are ionized in the ion source and then accelerated in the electric field to the energy of a few hundred kilovolts. The formed ion beam is directed at the surface of any material. The ions are introduced (implanted) into the substrate surface to a depth of about one micron. The kinetic nature of this process means that practically any material can be doped with any element. The biggest advantage of the ion implantation method is the lack of adhesion problems between the material and the modified layer. This is because there is no boundary between the substrate and the implanted material. The process itself does not involve the addition of a material layer, but rather the structure modification of the existing substrate surface [4].

The ion implantation method also has its limitations, mostly due to its inability to work with complex shapes. Structural changes with the doping material only affect the layer directly within the ion beam. In addition to the inability to modify complex geometric details, the relatively low penetration depth and high cost of implantation can be considered as the main disadvantages [4].

3. Viable catalytic surfaces

In-cylinder catalytic coating requires an additional step in the manufacturing stage of several engine elements. The key aspect of properly utilizing the potential of such catalysts is carefully to choose their location in the cylinder. Coating any surfaces that are subject to friction due to piston movement is not considered. Thus, one of the only universally viable options for catalyst-coated surfaces within the cylinder is the piston crown.

Other surfaces that can be coated with a catalytic layer depend on the type of engine. For CI engines a catalytic surface could be applied on the glow plug as well as the injector, whereas for SI engines only the spark plug can be coated for most engines, coating the injector is only possible for direct injection engines (Fig. 2). The choice of the element on which the catalytic coating is applied must consider the catalytic surface lifespan. Thus using easily replaceable in-cylinder elements, such as plugs and injectors, seem to be a much more economically reasonable solution. After all, changing the piston due to the wear of the piston head catalytic layer would be both costly and difficult, and thus not economically viable as an application.

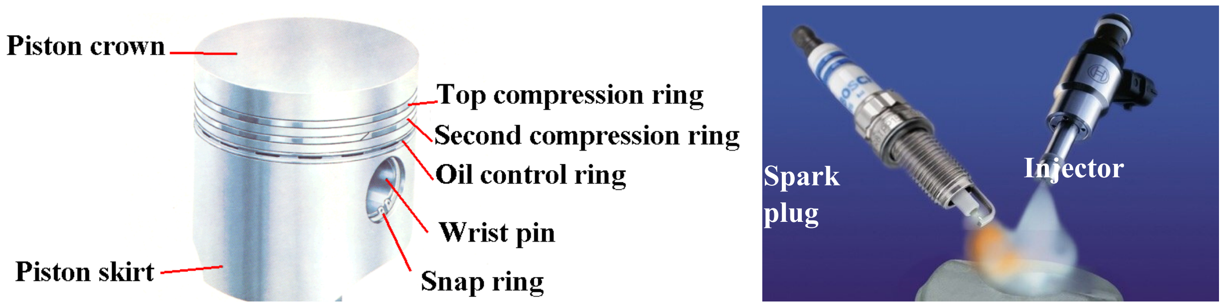

Fig. 2. The most likely surfaces for catalytic coating

Placing the catalyst on the surfaces of glow/spark plugs and injectors significantly reduces the required minimum lifespan of the in-cylinder catalytic layer, from the lifespan of the entire engine assembly down to the lifespan of injectors and glow/spark plugs, which are replaced more often than pistons, most commonly during vehicle tune-up (Fig. 3). Since the regular service intervals for spark plugs are between 60 000 – 80 000 km this also needs to be the lifespan and durability of the catalytic layer. Putting the catalyst on replaceable in-cylinder parts makes the in-cylinder catalytic solution much more realistic, with necessary catalytic layer durability comparable to what can currently be achieved through the most effective coating methods.

Fig. 3. Replacing spark plugs, glow plugs, and injectors is much easier to perform than replacing piston elements

The most beneficial effect of using easily replaceable engine parts as catalytic surfaces is the possibility or using this new solution in older vehicles that need it the most. The largest contribution of vehicle emissions comes from older vehicles (usually diesel vehicles) that meet Euro 3 or 4 standard in the age of Euro 6b and Euro 7. Because the emission limits change so quickly, there are still many vehicles, which have been produced and designed with much less stringent emission limits in mind. The considered in-cylinder catalytic solution can have a very significant positive impact on reducing HC emissions from older engines, and it can be achieved by simply changing the glow/spark plugs and injectors to their new replacement parts, which have been coated with a catalytic layer. Thus bringing in-cylinder catalysts to vehicles that were not designed for such solutions. This could prove to be a much easier and more affordable form of retrofitting for older vehicles in comparison to all of the currently available options.

4. Results

The study by Zu and Ladommatos [2] concerned the emissivity assessment of a platinum-rhodium-plated internal combustion engine. The researched object was a single-cylinder SI engine. A 0.15 mm thick catalyst layer was applied in the process of plasma spraying. Hydrocarbon and nitrogen oxide concentrations (Fig. 4-7) were measured at full engine load, constant crankshaft rotational speed of 1500 and 2000 rpm, and variable air to fuel ratio (Φ).

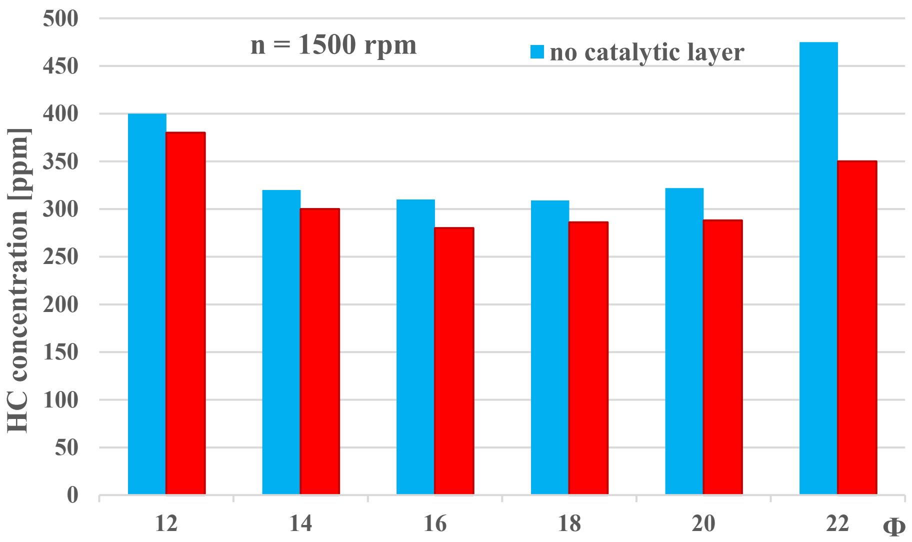

Fig. 4. HC concentration change at engine speed of 1500 rpm due to the effect of the catalytic surface

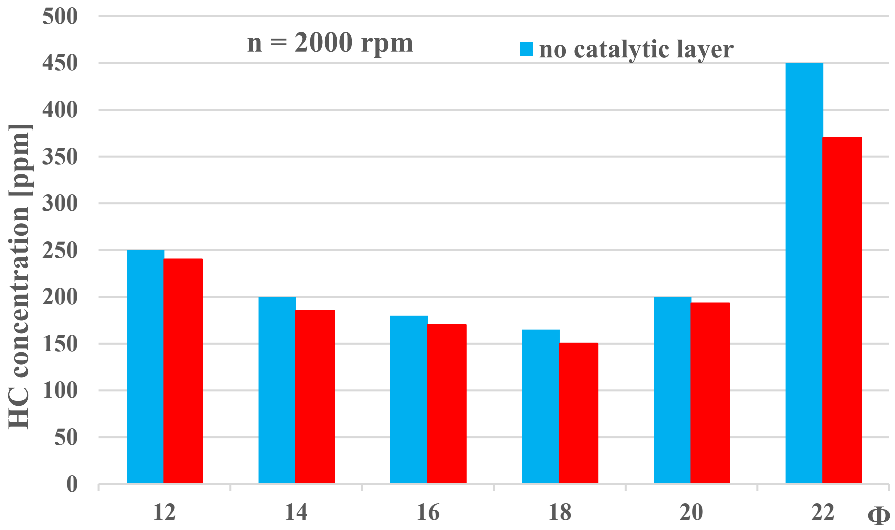

Fig. 5. HC concentration change at engine speed of 2000 rpm due to the effect of the catalytic surface

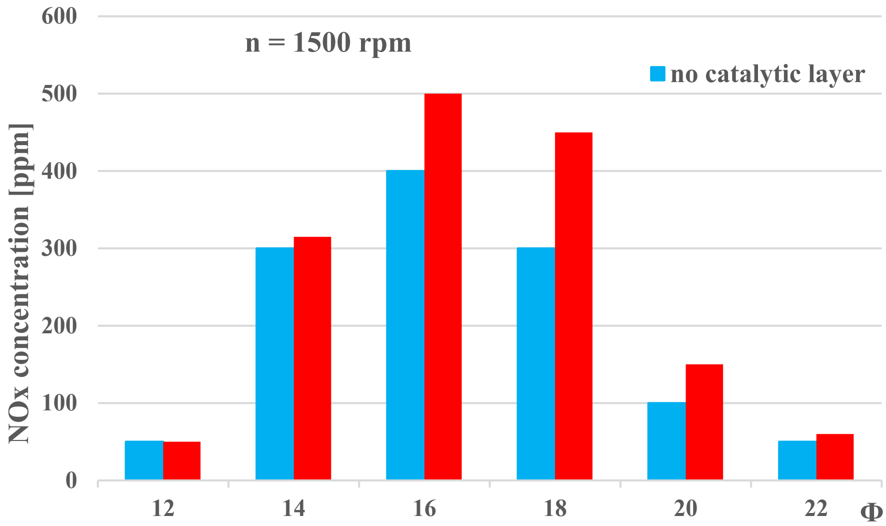

Fig. 6. NO_x concentration change at engine speed of 1500 rpm due to the effect of the catalytic surface

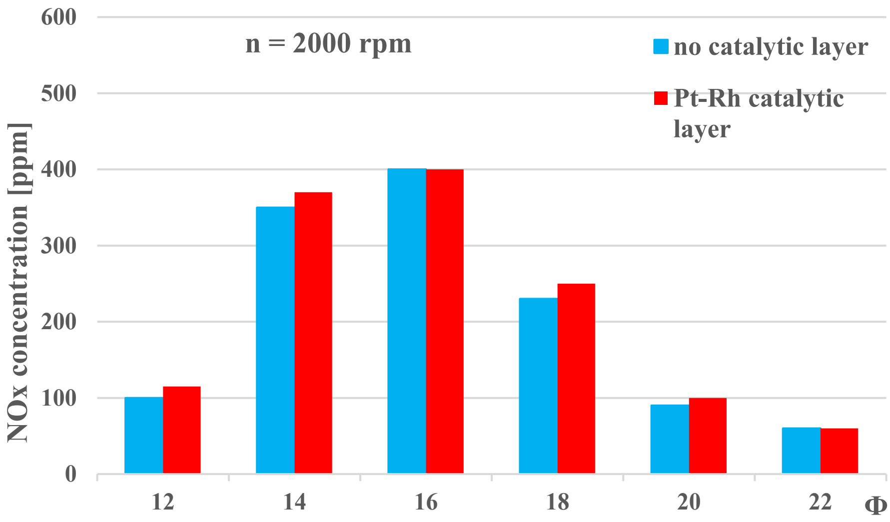

Fig. 7. NO_x concentration change at engine speed of 2000 rpm due to the effect of the catalytic surface

The obtained results indicated:

- a reduction of hydrocarbon concentration at engine speed equal to 1500 rpm by about 20% as a result of catalytic oxidation,
- slight decrease in hydrocarbon concentration at the engine speed of 2000 rpm,
- an unfavourable impact of the catalytic layer on the nitrogen oxides concentration at crankshaft rotational speed of 1500 rpm – average increase of 10%,
- no significant changes in the nitrogen oxides concentration at engine speed of 2000 rpm.

Further tests [2] measured hydrocarbon and nitrogen oxides concentrations according to the cooling fluid temperature (Fig. 8 and 9).

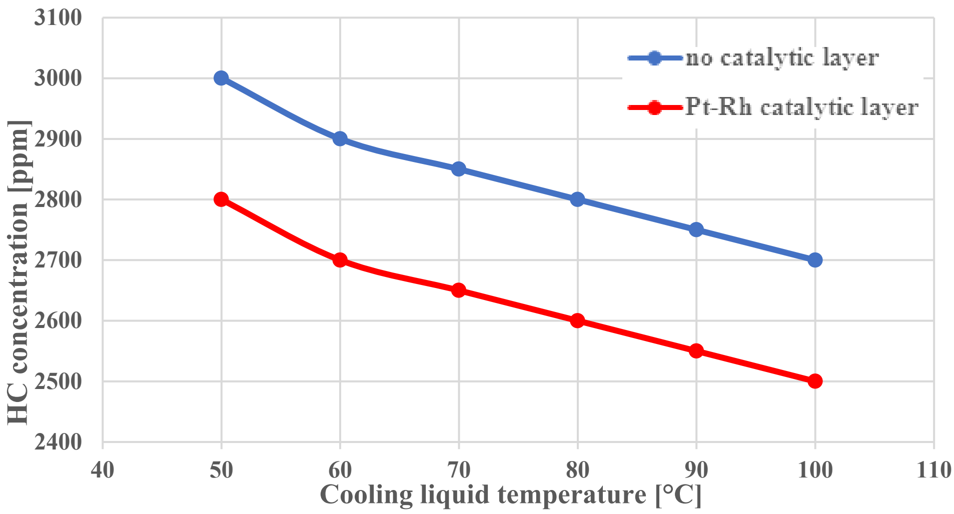

Fig. 8. HC emission change as a result of the catalytic surface at different coolant temperature values

The performed measurements revealed a linear relationship between hydrocarbon concentration and the coolant temperature. The use of a catalytic surface reduced the hydrocarbon concentration by about 10%. This indicates that the catalytic oxidation efficiency, resulting from the presence of a catalyst inside the engine, does not depend on the engine temperature. On the other hand, the concentration of nitrogen oxides increased due to the increase of the maximum temperature inside the cylinder, as a result of the catalytic processes. The intensification of the above phenomenon does not depend on the engine temperature.

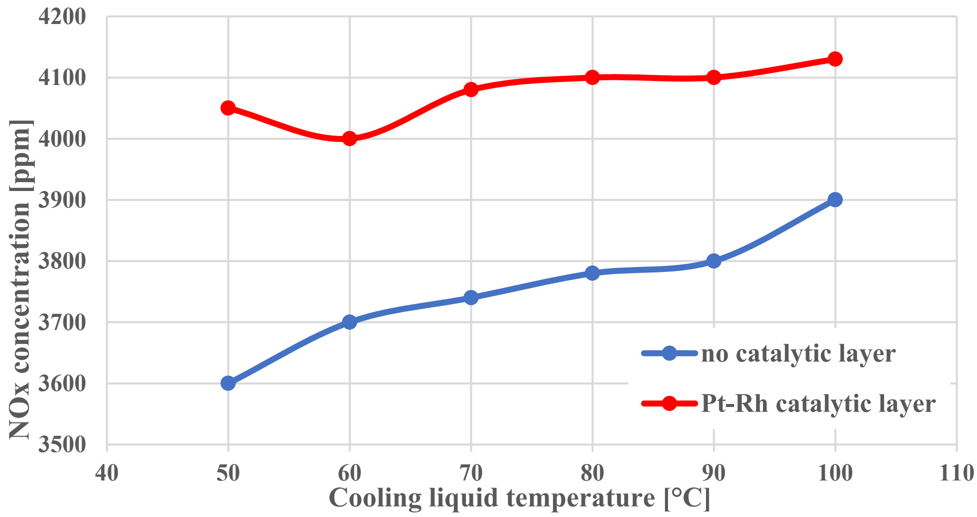

Fig. 9. NO_x emission change as a result of the catalytic surface at different coolant temperature values

5. Conclusions

Legislative changes and increasingly stringent emission standards result in the search for new technical solutions that would limit the harmful emissions from internal combustion engines. Apart from the use of advanced exhaust aftertreatment systems, it is necessary to seek solutions to limit the very formation of harmful compounds in the combustion chamber itself. Based on a performed review of the application of in-cylinder catalyst layers, it has been found that they are a technical solution that can effectively limit the formation of harmful compounds in combustion engines. The life span of a catalytic surface depends on its application technology. Plasma spraying is the most common and most readily available, but in the context of catalytic coating life it does not work as well as ion implantation, indicated as a high potency solution in this aspect. The catalytic layer lifespan requirements are partially dependent on the choice of surface on which the catalytic layer is applied. Using surfaces of easily replaceable in-cylinder parts for the application of the catalytic layer may allow the use of cheaper layer application technologies offering shorter layer lifespan.

While the use of in-cylinder catalysts will not single-handedly solve the emission problems of modern vehicles, it can be considered a significant milestone in emission reduction of vehicles with combustion engines. In-cylinder catalytic reduction of hydrocarbons (HC) should be the first step of a modern vehicle's exhaust emission of reduction system, and it should be supported by the remaining elements of the aftertreatment system. In vehicles with CI engines, this can include a secondary Diesel Oxidation Catalyst (DOC) aimed at reducing CO and the remaining hydrocarbons after reaching its operating temperature, a Diesel Particulate Filter (DPF) for particulate matter, and Selective Catalytic Reduction (SCR) using ammonia for the reduction of NO_x. It is important to note that all of these solutions are additive, and thus must be employed together for maximum effect. In-cylinder catalyst may not necessarily always be a replacement of the current DOC aftertreatment systems, but it can improve the exhaust emission of the vehicle in the engine operating ranges that were up until now left unaddressed due to the lack of need and interest. Such solutions can even find use in SI engines as the emission limits continue to decrease, especially in engines with direct injection systems, where the injectors are within the cylinder instead of the intake manifold. This can further reduce the emissions of particulate matter, through the reduction of HC in the exhaust gases, which has become a major issue for direct injection gasoline engines. It should be noted that the reduction of HC generated in the combustion chamber also indirectly decreases the production of CO and particles, and thus has a more significant impact on the overall emission of the vehicle.

References

[1] Guo, H., Murakami, H., Kuroda, S., *Thermal cycling behavior of plasma sprayed segmented thermal barrier coatings,* Materials Transactions, 47 (2), 306-309, 2006.
[2] Hu, Z., Ladommatos, N., *Reduction of unburnt hydrocarbon emissions from spark ignition engines using in-cylinder catalysts*, Proc Instn Meeh Engrs, Part D: Journal of Automobile Engineering, 210, 1996.
[3] Nedunchezchian, N., Dhandapani, S., *Effects of in-cylinder catalytic coating on the performance of a two-stroke spark ignition engine,* Indian Journal of Engineering & Materials Sciences, 8, 1-7, 2001.
[4] Neonila Levintant-Zayonts, Rozprawa doktorska, *Wpływ implantacji jonowej na własności materiałów z pamięcią kształtu typu niti.*
[5] Normand, B., Fervel, V., Coddet, C., Nikitine, V., *Tribological properties of plasma sprayed alumina–titania coatings: role and control of the microstructure*, Surface and Coatings Technology, 123, 278-287, 2000.
[6] www.pnc.pl/natryskiwanie-cieplne/natryskiwanie-plazmowe.html – 3.04.2017.
[7] Merkisz, J., Pielecha, J., Radzimirski, S. *New Trends in Emission Control in the European Union. Series: Springer Tracts on Transportation and Traffic*, STTT 4, ISBN-Print: 978-3-319-02704-3, ISBN-Ebook: 978-3-319-02705-0, Vol. 4, XII, 165 p., Springer, New York, USA 2014.