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SELECTED APPLICATIONS OF CARBON NANOTUBES IN CONSTRUCTION OF INTERNAL COMBUSTION ENGINE

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Abstract

For over hundred years the internal combustion engine has been applied as the drive of various vehicles and it is continuously improved. The most important requirements that should be satisfied by future engines concern reduction in fuel consumption and exhaust emissions preserving possibly low cost of engine manufacturing. In order to fulfill such demands a concept of so called "downsizing" has been proposed which concept is based on high values of mean effective pressure, and as a consequence high mechanical and thermal loads. Further increase of engine power per liter is still possible but new materials are needed in order to keep the manufacturing costs at the reasonable level. The paper presents an analysis of operational conditions of selected parts of supercharged engines constructed according to the downsizing concept and shows areas where the use of new materials could be most profitable. Results of engine tests carried out using modernized catalytic reactors and pistons in which advantages of the carbon nanotubes unique properties were deliberately taken have been presented in this paper as well. The obtained results allow to conclude that the nanotube layer over the piston skirt offers the friction losses reduction by as much as 16% relative to the whole engine. The observed properties of nanotubes can be profitable in a number of applications indicated in the paper.

Keywords: *carbon nanotubes, combustion engines, catalytic converter, friction*

1. Introduction - carbon nanotubes vs. other allotropic forms of carbon

Carbon nanotubes are one of numerous allotropic forms of carbon like graphite, diamond, fullerenes, graphene and amorphous one. These allotropic forms differ diametrically one from

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another in physical and chemical properties. These differences result from three-dimensional crystalline structure of carbon atoms and their mutual influence. The structure of some carbon allotropic forms has been presented schematically in Fig. 1. The carbon nanotube in this figure is a Single Walled Carbon Nanotube of simplest structure; prevailing form are the Multi Walled Carbon Nanotubes composed with concentric single walled tubes of different diameters. Both varieties of nanotubes of length within a several nanometers to several micrometers range can be obtained through an adequate selection of synthesis parameters. Commonly, the diameter of single walled nanotubes is 1 to 2 nm, while the diameter of multi walled nanotubes is 2 to few dozen nm and the distance between consecutive coaxial layers is constant, and equals 0.36 nm [5].

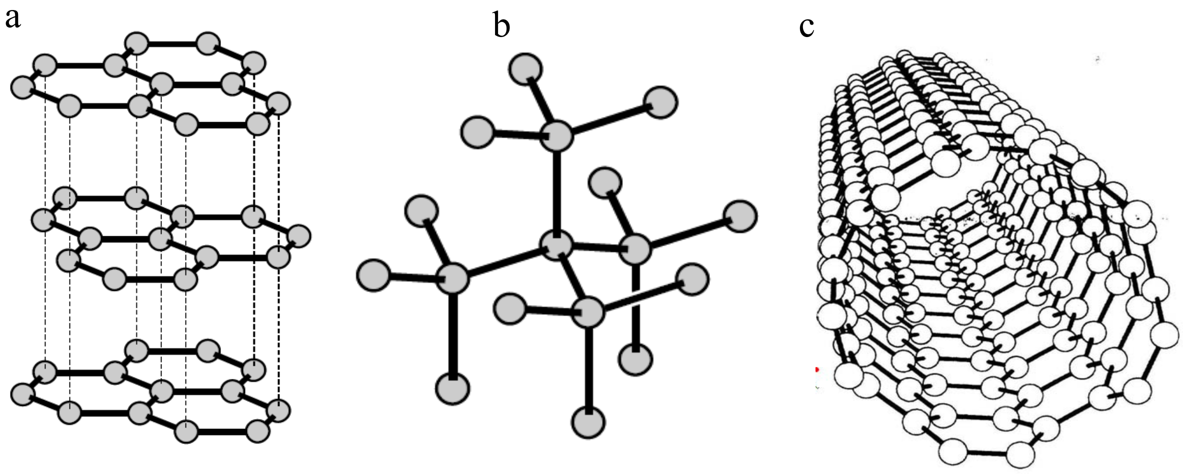


Fig. 1. Crystalline structure of graphite (a), diamond (b) and carbon nanotube (c)

Graphite, diamond and amorphous form of carbon - sometime defined with DLC abbreviation (Diamond like Carbon) found a well established industrial application also in construction of internal combustion engines [28]. In principle, the carbon nanotubes are the subject of intensive applicability tests and their industrial applications are still relative rare [3,8]. An intensification of carbon nanotubes production makes that their price goes down by about a half every year [5] and is no more an obstacle in industrial applications. The authors have not come across papers of independent scientific teams that would present results of tests on carbon nanotubes applications to the IC engines. The nanotubes properties presented in numerous reports from non-engine research prove that undertaking such efforts is more than justified. In particular, when carbon nanotubes are applied as a layer of catalytic converter, the achievements described in [2, 6, 11, 14, 15, 17, 20] are worthy of notice. Application of nanotubes to the piston skirt surface is a consequence of results presented in [1, 7, 9, 16, 18, 19, 23, 24, 25, 26, 27, 29] as the outcome of tests on use of nanotubes to reduction of friction on macro scale objects. Tests discussed in further part of this paper were carried out within the N 509 052 32-3940 (Highly effective catalytic converter on the basis of three-dimensional hierarchic carbon nanostructures) and N 502 511240 (Effect of nanotube layer over a piston skirt on proecological properties of IC engine) projects. The aim of the presented study was the recognition of profits due to the application of carbon nanotubes in construction of selected parts of IC engine. Expected demands towards the passenger car engines were taken into consideration in particular.

2. Trends in piston IC engines design

IC engines found a great number of well established applications in industry and transport, though a dominating majority is dedicated to car drives. A procedure of new solutions implementation requires about ten years in automotive industry and involves successive collaboration of R&D, quality control and setup departments. When choosing the application area for carbon nanotubes one should consider not the engines produced to-day but those which are supposed to be produced in ten years.

In the nearest future the direction of engine development will be determined by the "downsizing" concept, which leads to the increase in break mean specific pressure and specific power indexes. Ecological conditions and more stringent emission standards introduced also in the developing countries will play considerable role at the same time [4,13].

To make the "downsizing" highly profitable concept an achievement of high power and torque from an engine volume unit is most desirable. This goal could be accomplished both by spark and compression ignition engines by the use of supercharging, especially the sequential one. An unavoidable result of supercharging is higher thermal and mechanical loads, especially of the crank system elements. Fig. 2 presents the operational parameters of SI engine sequential supercharged during the acceleration test to 60 kph at the highest gear. One should notice the ignition delay present several degrees after TDC which prevents knocking but simultaneously leading to the increase in normal forces acting upon piston skirt. Further development of such constructions requires the use of low friction materials such as carbon nanotubes. Wider analysis of IC engines development exceeds the frames of presented paper but can be found in literature, e.g. in [13].

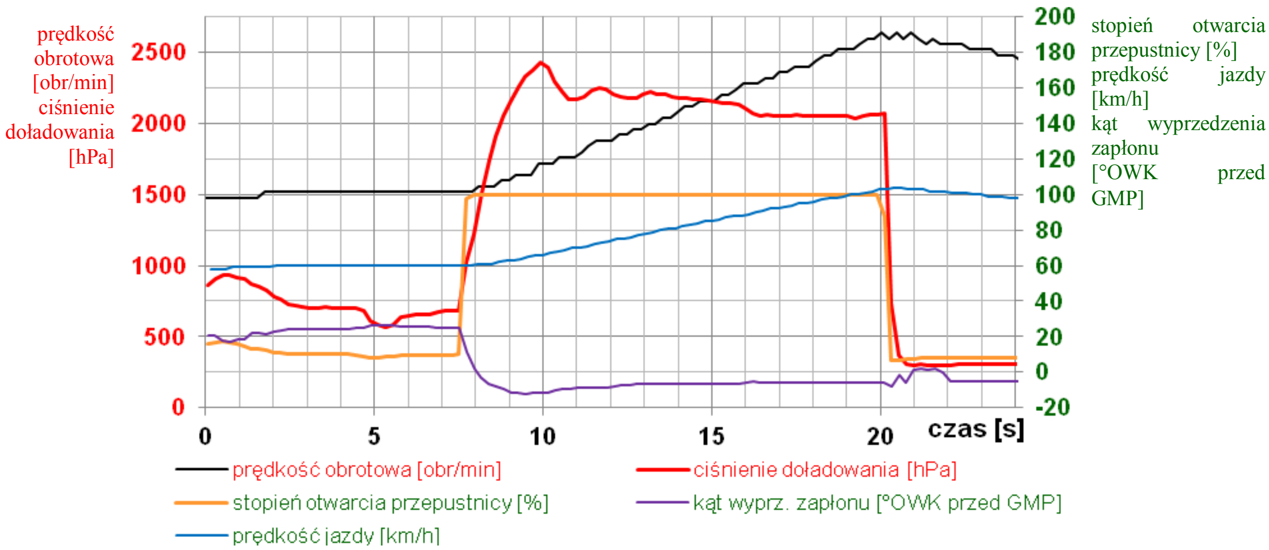


Fig. 2. Driving speed and engine selected parameters recorded during a road acceleration test from 60 kph; Volkswagen Golf TSI, BMY engine, classic gear box; colors of quantities in legend correspond with the ordinate axis

3. Concept of experimental catalytic converter with a layer of carbon nanotubes

The operation of standard catalytic converter consists in redox reaction of carbon monoxide and hydrocarbons present in engine exhaust which is possible due to catalytic properties of platinum covering metal or ceramic monolith. Efficiency expressed as the conversion rate depends mainly on the surface of contact between platinum and exhaust.

On macroscopic scale the increase in contact area can be achieved by the suitable structure – possibly high number of canaliculus. On microscopic scale each canaliculus should have rough and highly developed surface. On standard converter this goal was achieved by the application of washcoat which is a carrier for the catalytic materials. Few grams of platinum are used on average in oxidizing catalysts installed in car exhaust systems [10].

The carbon nanotubes were applied as a washcoat on experimental research converter. Main factors that inspired application of nanotubes to experimental catalytic converter were as follows:

- According to carried out tests [5] physical and chemical properties of nanotubes allow to believe that they would not be destroyed in conditions inside oxidizing converter.
- Large area and three-dimensional structure could facilitate contact with exhaust. Exemplary photo of nanotubes surface obtained by a transmission electron microscope is presented in Fig. 3.
- An increase in platinum activity at a presence of nanotubes resulting from the higher ionic conductivity of nanotubes.
- Literature widely presents similar applications of carbon nanotubes in filters and chemical reactors [5]. Particularly important are the tests with catalytic fuel cells where platinum combines with carbon nanotubes. Numerous authors maintain that the application of nanotubes and carbon fibers could increase the catalytic activity of platinum used for construction of fuel cells [21].

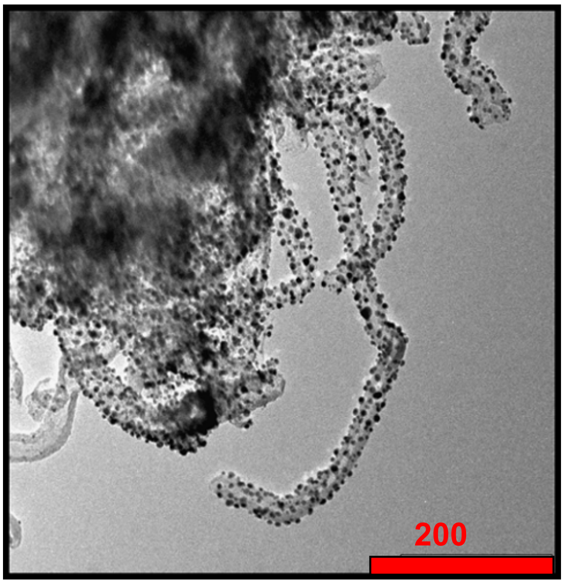


Fig. 3. Carbon nanotube layer with spot deposited platinum nanoparticles, picture recorded by the LEO 922A transmission electron microscope [22]

Standard ceramic monolith was used to construction of experimental catalytic converters but their volume was limited to just 200 ccm, which is several less than in standard converters. Three stages could be distinguished within the process of converter preparation:

- development of monolith,
- synthesis of nanotubes
- preparation of nanotubes surface functionality
- deposition of platinum coating.

This process was described in details in [13]. Omitting technological details it should be noted that weight of platinum used for this experimental converter was at least 100 times less than typical applied in oxidizing catalytic converters of contemporary passenger cars.

4. Results of tests on experimental catalytic converter with carbon nanotubes layer

The catalytic converters constructed on site were subjected to a series of tests at physical-chemical lab, engine test shop and chassis dynamometer. Visual inspection proved that the obtained test converter fulfills introductory requirements as the platinum and nanotube layer structure is concerned. A catalytic activity relative to carbon monoxide has been proved. Tests carried out at physical-chemical lab could not reconstruct fully the conditions in engine tail pipe. Due to that a key role play suitably planned engine dynamometer tests. Primary tests were carried out at the Combustion Engine Laboratory of the Poznań University of Technology and the experimental converters were installed in the exhaust system of VW TDI engine. A view of engine with hooked up catalytic converter is presented in Fig. 4.

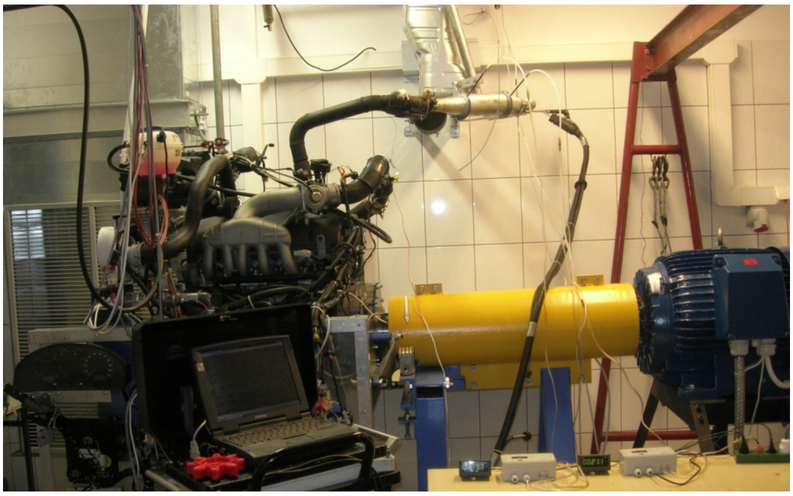


Fig. 4. A view of the TDI engine on test stand during tests on carbon monoxide conversion ratio [13]

The experimental catalytic converter was installed parallel with a standard one in exhaust system of engine which facilitates comparison of two converters efficiency measured by the carbon monoxide conversion rate. The way both converters were installed was presented in Fig. 5.

Tests on several versions of experimental converters marked with successive letters were carried out for several operational points described with rotational speed and fuel dose. Carbon monoxide concentration in exhaust before and after the catalytic converter was measured with the Testo Emission Analyzer. Results of carbon monoxide conversion rate calculations obtained for selected converters were summarized and presented in Fig. 6.

Fig. 5. A view of the exhaust system with a standard oxidizing converter (black housing) and experimental converter (silver housing) connected parallel [13]

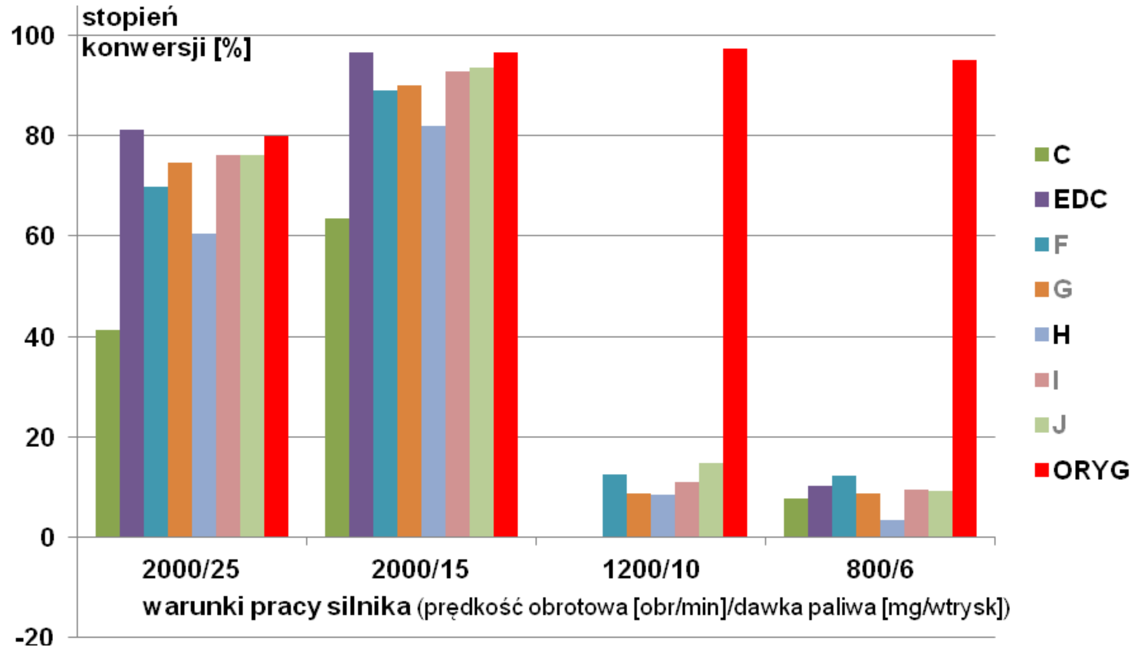


Fig. 6. Carbon monoxide conversion ratio determined for experimental converters and original one ("ORYG"), standard fitted to an investigated engine of Volkswagen Transporter

The conversion rate of catalytic converters was investigated using a non-homologated method but analyzing the sources and values of random errors one can conclude that the adopted procedure and applied instrumentation allowed to achieved the anticipated goal.

Catalytic activity towards the carbon monoxide was demonstrated for all converters tested. However various rates of conversion were achieved for individual converters, all of them were highly dependent on engine operational conditions. The highest rate of conversion was obtained for multisectional converter consisting of three monoblocks – E, D and C – put into common housing. At the operational point corresponding to medium and high engine load this converter showed the highest rate of conversion among all experimental converters tested. The EDC converter presented the conversion rate the same or even slightly better than much bigger standard converter.

At the operational point corresponding to low load and low speed all experimental converters presented unsatisfactory values of the carbon monoxide conversion rate. Supplemental tests proved that the common drawback of all experimental converters was high light-off temperature; the EDC converter gives 50% conversion rate at about 280 °C . This problem has not been solved yet.

In order to carry out all tests planned each of converters was installed in exhaust system of the VW TDI engine running several hours under high load when the exhaust temperature exceeded 400 °C . The decrease of toxic compounds conversion rate determined for individual converters was not observed during successive measurements. Therefore one can assume provisionally that the carbon nanotubes are not subjected to destruction in the environment of engine exhaust, but the experiments carried out can not replace the durability tests in conditions of regular operation and long mileage.

5. Concept of experimental piston skirt covered with carbon nanotube layer

The knowledge of engine parts operational conditions and results of standard tests of piston skirt layers allow to estimate as probable the presence of several interaction mechanisms of nanotube layer over piston skirt on functional features of piston-cylinder group.

- Expected reduction in friction losses under conditions of mixed lubrication which results directly from properties of carbon nanotubes. Additionally, nanoparticles of friction modifiers as molybdenum disulfide can be introduced into nanotubes structure.
- Grindability of nanotubes superficial layer, which is not directly bound to piston material could protect engine against seizure.
- Formation of nanotube layer that would be intensively ground at the run-in stage will lead to their dispersion in lube oil. Results discussed in Chapter 5.2.3 prove that even low concentration of nanotubes in lube oil favorably increase its lubricating properties. This effect could be seen in every kinematic node supplied with oil.
- Reduction in friction losses at the full film lubrication regime which results from oil flow properties through a nanostructural near-wall flow.
- Reduction in forces connected with piston secondary motion and their implications like surface wear, vibrations and noise.
- Secondary limitation of friction losses resulting from intensive piston secondary motion facilitating adjustment of other parameters like piston pin axis shift.

A view of the experimental piston with skirt covered by the layer of carbon nanotubes has been presented in Fig. 7.

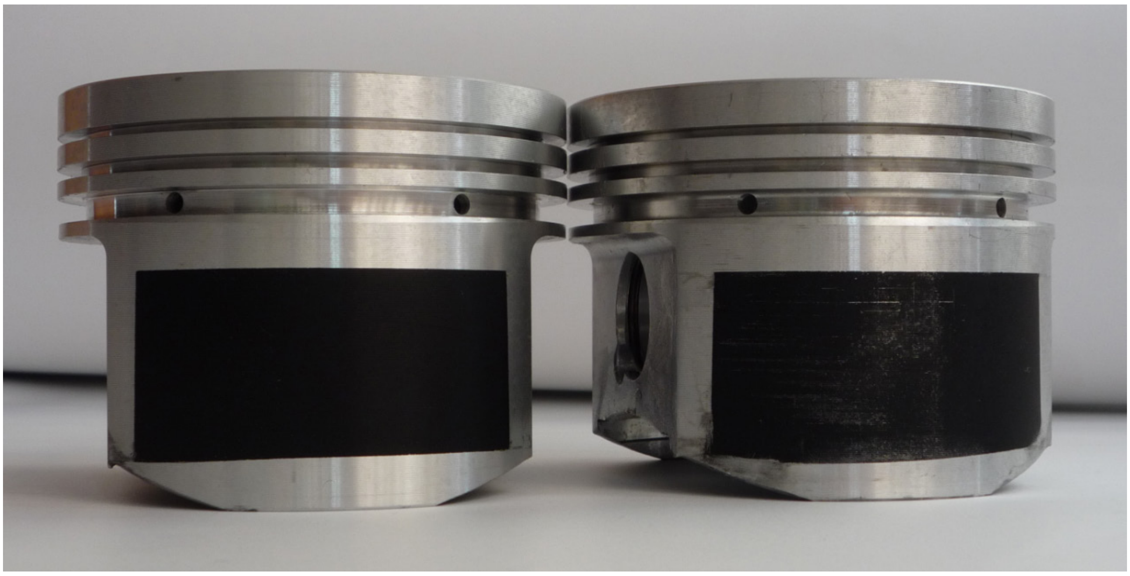


Fig. 7. Experimental piston with nanotubes covered skirt; view taken before and after engine tests

Because of problems complexity the measurements and tests were divided into four stages:

- first stage – piston measurements before covering with nanotubes
- second stage – piston measurements before fitting on engine
- third stage – engine tests
- fourth stage - evaluation of wear.

The aim of piston measurements was determination of shape and surface roughness deviation and it was broadly described in [12, 13].

The engine tests were carried out after fitting pistons on a purposely constructed test rig with a two-cylinder engine driven by an electric motor. This test rig, called simulation stand, serves for possibly precise reconstruction of engine crank system real operational conditions with concurrent torque measurement when engine is externally driven. The camshaft on this engine has been inactivated with closed valves as well as water and oil pumps driven by the crankshaft. The latter two were replaced by electrical driven external pumps.

These changes made that each revolution of crankshaft forces a repeated cycle of compression and expansion while a part of charge blows by to the crank case because of leakiness. When the valves are closed a possible leak can be made up by additional one-way valves called charge make up valves and installed instead of spark plugs. Test stand construction allows for valve closing or opening in order to aspire freely ambient air or compressed air supply. Compressed air supply to the cylinder at the beginning of compression stroke leads to higher cylinder pressure. This can serve for simulation of real engine higher loads.

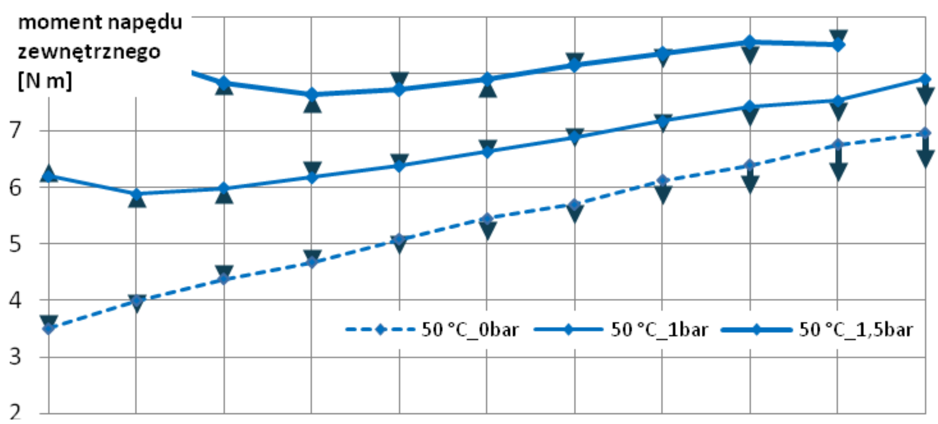
6. Test results

Only elements of crank mechanism are driven by the external drive on the modified engine and therefore a precise definition of friction losses is possible by the measurement of external drive torque. Following significant factors affecting the measured torque can be distinguished:

a) friction losses occuring between piston skirt and cylinder liner, which are analyzed in this paper,
b) friction losses generated between the ring pack and cylinder,
c) friction losses in crankshaft bearings,
d) loss of compressed charge as a result of blow-by as well as thermal losses originated in heat transfer between charge and surroundings.

It can be assumed that keeping the piston diameter unchanged the nanotubes cover over piston skirt does not affect substantially the phenomena mentioned in points b to d, causing considerable change in external torque balance. Therefore a comparison of torque values recorded in similar conditions for engine with standard pistons and the one with pistons covered with nanotubes facilitate the determination of nanotube layer effect on friction losses.

The torque has been recorded at a frequency of 9.6 kHz and gave 20 thousand successive results. Therefore every measuring file contains information on torque course within 2 seconds; the mean value has been calculated on the basis of such course.



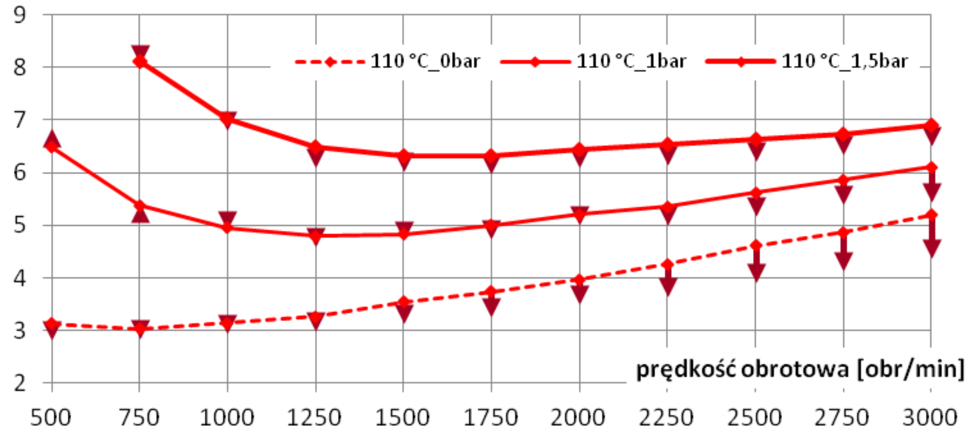


Fig. 8. Standard pistons friction losses courses and marked with pointers changes recorded after replacement of standard pistons with experimental ones with carbon nanotubes covered skirt

Three main measuring series, defined by the oil temperature 50 °C, 80 °C and 110 °C can be distinguished in the program. Within every superior series another three series relative to the pressure before charge supply valves can be distinguished, namely 0 bar, 1 bar and 1.5 bar. These series correspond consecutively to valves closed[1], open (connected to ambient air) or connected to the compressed air installation with 1.5 bar of absolute pressure. Each measuring series – of total nine – consists of eleven points defined by rotational speed variable within the range from 500 rpm to 3000 rpm with a 250 rpm step. The whole program consists of 99 measuring points and was carried out on the engine with standard pistons. The measurements were repeated on the engine with experimental pistons. Results obtained for extreme values of oil temperature are presented in Fig. 8.

The application of carbon nanotubes on piston skirt caused a considerable reduction of friction losses expressed by decreased external torque reaching even 16% in most favorable conditions of engine run. I should be noted that presented difference relates to the total friction losses that take into account not only losses on piston skirt but also those generated by the ring pack and slide bearings. Data available in literature prove that three kinematic pairs mentioned here are comparable when friction losses are taken into consideration. Because of that the reduction in friction losses recorded after application of pistons with modified surface are surprisingly high.

After finished engine tests the experimental pistons were removed and samples were taken from their surface which was eventually investigated with a transmission electron microscope of high resolution. Fig. 9 presents an exemplary view of piston skirt section with a nanotube layer; analysis of all samples tested allow to conclude that carbon nanotubes have not suffered destruction during engine tests.

[1] Closing of charge supplementing valves actually brings about certain negative pressure but it is not a perfect vacuum; the 0 value was assumed in order to simplify notation of measurement files. Here, it means only that the charge is not supplemented.

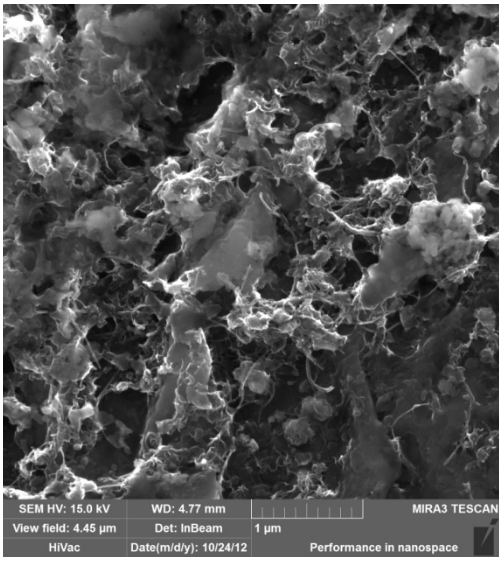


Fig. 9. A view of carbon nanotubes on a sample surface of piston removed from engine; picture taken by a high resolution transmission electron microscope (HRTEM)

7. Conclusions and final remarks

Construction of prototype, experimental oxidizing catalytic converters and pistons, and eventual tests show a considerable functional advantages resulting from application of carbon nanotubes. In a case of catalytic converter it has been shown that:

- carbon nanotubes are not destruction prone under operational conditions of oxidizing converter dedicated to diesel engine,
- the developed surface of nanotubes allows for a significant limitation of applied platinum, though such converter demonstrate high light-off temperature,
- technology of converter has been developed that could be implemented in mass production.

Tests carried out on pistons allow to formulate following conclusions:

- carbon nanotubes over piston skirt do not disintegrate,
- nanotube layer on piston skirt gives considerable reduction of friction losses within a wide range of engine operational conditions,
- technology used for manufacturing of experimental pistons could be improved and eventually applied to the mass production.

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