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THE INVESTIGATION OF EXPERIMENTAL COMBUSTION ENGINE ELEMENTS CONDUCTED WITH USE OF ATOMIC PHYSICS METHODS

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Abstract

The authors put forward in earlier publications the concept of using carbon nanotubes (CNT) in order to improve the functional characteristics of selected structural components of internal combustion engines. The main goal of applying carbon nanotubes is to take advantage of its unique properties, which cannot be found among traditional construction materials, to reduce emissions and fuel consumption. To achieve this goal it is essential to come to know about elements and materials behaviour in specific application, for example piston or catalytic converter. In this article, selected methods in the field of atomic physics applied to the study of experimental engine components produced using nanotechnology are presented. For example, the electron microscopy in conjunction with registration of the characteristic X-ray and Raman spectroscopy were used. These test methods are improving the knowledge of the properties and design of pistons and catalytic converters with surface coated with multi-walled carbon nanotubes. The results of elements surface analysis, which were diverted from the engines after a series of test stand investigations, offer insight into the processes that take place in layers of carbon nanotubes in actual engine operating conditions. The knowledge gained with application of atomic physics methods allows achieving further improvement of carbon nanotubes layers and its functional characteristics.

Keywords: *combustion engine researches, carbon nanotubes, electron microscopy, Raman spectroscopy*

1. Introduction

Carbon nanotubes (CNT) are an example of a new group of materials and have unique physical properties, in some respects considerably more favourable than the properties of any other materials known so far. For example, the strength of selected varieties of carbon nanotubes on stretching is several times higher than the strength of top steels [3]. Among other properties, carbon nanotubes are characterized by a high ratio of lateral surface area to volume and favourable tribological properties, permitting reduced friction.

The first of these characteristics of carbon nanotubes predestined for use in the construction of catalytic converters. In this case, the catalyst nanoparticles, for example platinum, are applied to the surface of the CNT. Strongly developed lateral surface of the nanotubes increases the surface area of the catalyst in contact with the environment in chemical reactions occur. This concept has been used in many different applications of reactors [12, 19, 24, 26] and in the air purification systems in cabins, NASA operated spacecraft [4]. The authors present the results of earlier publications on the desirability of the use of carbon nanotubes as an intermediate layer in the oxidising catalytic reactors used in the exhaust systems of diesel engines [15].

Preferred tribological properties of carbon nanotubes have been discovered and confirmed in a series of experiments conducted both in the nanometre scale, the individual carbon nanotubes [11, 17, 18] and the nanotubes in the macroscopic properties [1, 5, 22]. In the paper [15], the results of an extensive research project indicating the possibility of a significant reduction in friction losses of combustion engine by coating a layer of carbon nanotubes on bearing surface pistons are presented.

It should be noted that the industrial applications of carbon nanotubes is very limited, although it is clearly demonstrated that nanotubes are superior in terms of number of key mechanical properties of all previously used construction materials. Broader analysis of the obstacles to the use of nanotubes in bulk products are presented in publications [2, 6]. Among the factors that inhibit the use of nanotubes may be mentioned the need for further knowledge of their impact on the environment, especially on the human body [25].

The authors of this publication consider it is purposeful to emphasize that an industrial use of any construction material − including carbon nanotubes − is not determined by how much material is superior to others in terms of the selected features. Engineering application requires that the material has a set of features, suitable for the requirements of the functional characteristics of the structure in which it is to be used.

The carbon nanotubes come in many varieties, which differ from each other significantly in terms of physical properties. These properties may also be modified by targeted selection of the nanotube synthesis conditions. Optimal use of nanotubes properties in selected applications − some of which are the subject of these article motor applications − requires testing to identify the phenomena occurring in the layers of nanotubes. For this purpose, it is necessary to use new methods of research, so far generally not applicable to internal combustion engines.

2. Functions of coatings on piston bearing surface

The coatings are applied on the piston-bearing surface of almost all modern supercharged engines. The original purpose of their use is primarily to avoid piston seizure of the following extremely unfavourable operating conditions:

- locally reduced clearance of the piston caused by deformation resulting from thermal and mechanical cylinder loads,
- reduction of the piston clearance following overheating,
- insufficient oil film thickness during engine start,
- deterioration of oil parameters due to high temperature, oil dilution by fuel or aging oil and impurities,
- condition of the engine before the end of the running in process.

Standard layers include graphite dissolved in a polyamide-imido resin, are applied by screen-printing and cured at high temperature. An example is the commonly used coating under the commercial name Grafal 255, comprising about 35% graphite and no other friction modifiers additives. New types of coatings containing molybdenum disulphide (type Evo Glide) and other friction modifier compounds [9]. The test results presented in the trial [16] confirms the possibility of obtaining very beneficial effects through the use of molybdenum disulphide.

The influence of the layer type covering the piston-bearing surface for wear of the surface and the friction loss is the subject of intensive research [7-9]. The results of these studies clearly confirm the positive role of the standard coatings to reduce the possibility of scuffing of the piston in the cylinder and reduce the surface wear of the cylinder under normal operating conditions of the combustion engine. As a result of tribological tests carried out outside the engine also, the possibility of a significant reduction in the frictional force by coating aluminum alloy surface with mention layers was indicated. In the actual engine, operating conditions, the total friction losses depend primarily on fluid friction conditions and therefore the use of standard coating does not provide direct large benefits in reducing friction.

When the piston-bearing surface was coated by layer of carbon nanotubes, there was a significant, circa 16%, reduction in power of an external engine drive [15]. The results indicate the need for further knowledge of the phenomena occurring on the surface layers of carbon nanotubes and ultimately leading to a significant reduction in friction losses.

3. The visual researches of carbon nanotubes layer on a piston-bearing surface

The layers of carbon nanotubes were deposited onto the bearing surface of experimental pistons at the NanoLab, Inc. in Waltham, USA [14]. The aqueous solution was used [15].

The main aim of the study was to determine the impact of carbon nanotubes layer covering the bearing surfaces of the experimental pistons on the operating conditions of collaboration with the cylinder liner surface. Among many parameters, characterizing the phenomena occurring between the bearing surface of the piston and cylinder liner surface greatest importance is attributed to the loss of friction. The effects of carbon nanotubes application was assessed because of a comparison of the measured values of experimental and standard pistons friction losses. An essential part of the research was done on the model test stand of the internal combustion engine, enabling the measurement of friction losses.

In order to clarify the phenomena leading to the reduction of the experimental piston friction losses pictures of the carbon nanotubes layers surface were taken. The sample prior to microscopic testing was purified by acetone. The structure display of the tested layers required the use of a scanning microscope with a very high resolution (High Resolution SEM). Fig. 2 shows an example of one of the images obtained for a sample taken at the end of a piston engine test.

On the image reproduced on the left in Fig. 2 by a suitable magnification the ability to attach the foreign particles on carbon nanotubes surface can be observed. These particles in the technical assessment of images of the carbon nanotubes can be called as contamination, but from the point of view of the tribological properties of the carbon nanotubes layers are likely to play a positive role. These pictures confirm the ability of carbon nanotubes to attach on their surface foreign nanoparticles. This feature can be used for the deliberate introducing of the chemical compounds with proven favourable tribological properties.

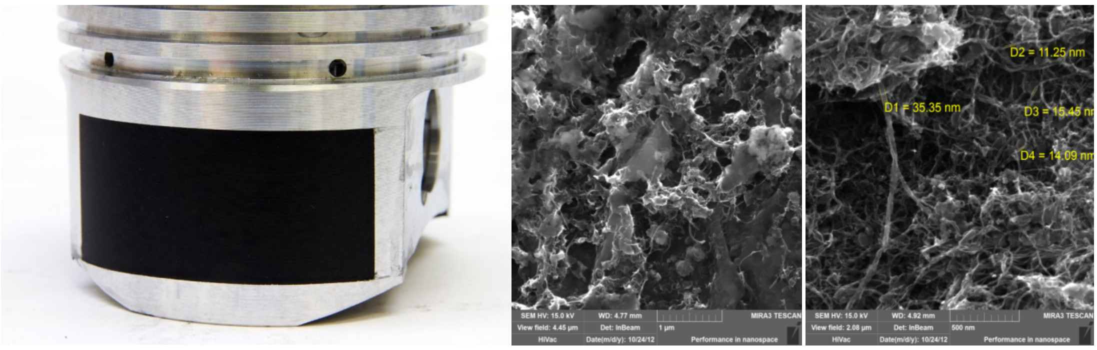

Fig. 2. The piston-bearing surface coated with carbon nanotubes layer; the pictures in macro scale and from scanning microscope obtained for sample from piston, which was dismounted from the engine after the researches at the test stand, were finished [15]

On the right side of Fig. 2 an image of nanotubes, forming a single layer on the piston-bearing surface is presented. These are multi-walled nanotubes with different diameters, for several nanotubes estimated values are applied to the image. The resulting image shows that carbon nanotubes are not destroyed under the physical and chemical environment occurring at the bearing surface of the piston.

4. Spectroscopic study of carbon nanotubes layers on the piston surface

In order to investigate the chemical composition of pollutants settling on the nanotubes layer on piston bearing surface during engine operation spectroscopic examination was performed. Spectroscopy of X-rays was used. The corresponding spectrum and evaluation of the chemical composition is shown in Fig. 3

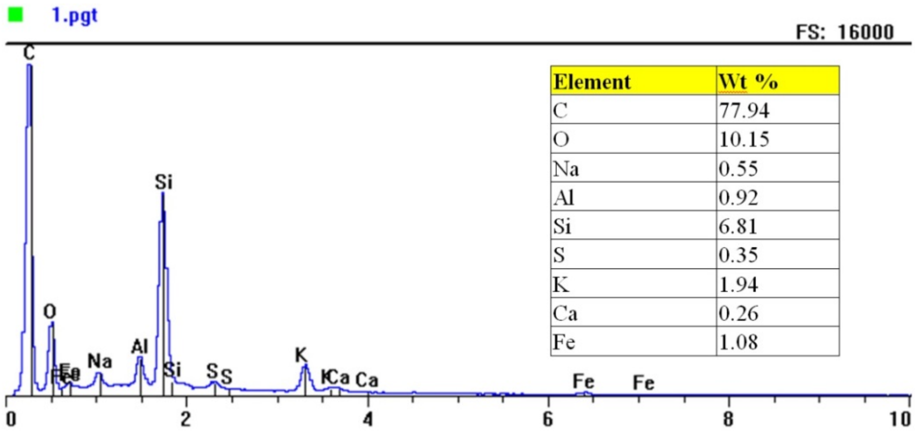

Fig. 3. Characteristic X-ray spectrum and chemical composition obtained for the surface layer of carbon nanotubes covering the bearing surface of the piston

On the surface of the sample stated, inter alia, the presence of silicon − about 6.8% of the mass share and potassium – 1.9%. These are the components of the varnish used for applying the nanotubes to a surface of the piston. The presence of iron indicates the bond of cylinder wall wear products with nanotube layer structure; interesting is to detect relatively large share of the mass of chemical compounds containing oxygen in their composition. It should be stressed that the X-ray spectroscopy allows determining the elements present in the sample, but by using this method, it is not possible to determine the type of chemical compounds that form these elements.

The researches show that the test surface is comprised of approximately 78% coal, but the result does not distinguish allotropic varieties of coal. This type of study cannot therefore be used to determine whether a sample is composed of carbon nanotubes or amorphous carbon. The more it is not possible to detect any defects of carbon nanotubes network, or their partial oxidation. This information may be obtained by using Raman spectroscopy [10, 13].

The analysis of the Raman spectrum obtained at different frequencies of inducement radiation allows determining the allotropic forms of carbon present in the sample. Radial breathing technique determines the diameter of carbon nanotubes in a sample. Raman methods with respect to the carbon nanotubes are currently being intensively developed, examples of results are shown in Fig. 4.

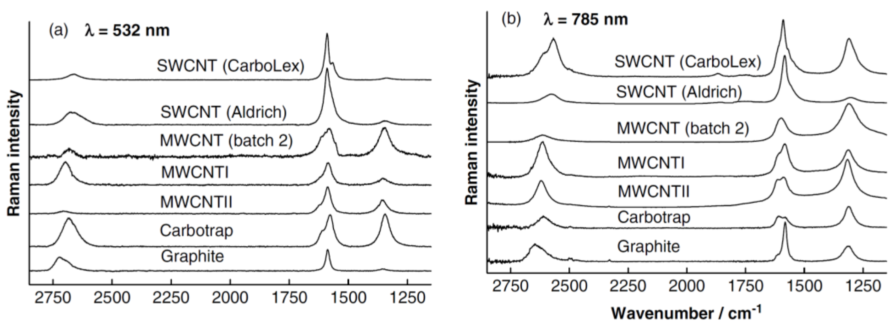

Fig. 4. Raman spectra obtained for the various allotropic forms of carbon for different excitation wavelengths (a: 532 nm; B: 785 nm) [13]

5. The function of carbon nanotubes in the design of an oxidation catalytic reactor

The function of the standard catalytic reactor is based on the oxidation of carbon monoxide and hydrocarbons contained in the exhaust gases. This is possible due to the catalytic behave of the platinum coating on the ceramic or metal carrier. The effectiveness of the reactor, expressed by the conversion ratio, is mainly determined by platinum surface contact with the exhaust gases. In the macroscopic scale, the increase of the contact surface is obtained by giving the carrier an adequate structure – the largest possible number of a small diameter channels. On a microscopic scale, each of the channels should have the most roughened surface area. In the standard design of the reactor, the increase of the platinum contact area with the exhaust gases is achieved by applying an intermediate layer – washcoat. On its surface, the platinum is applied and acts as a catalyst. The oxidation reactors for motor industry use a few grams of platinum on average [23].

The experimental design of research reactor used carbon nanotubes serving as a washcoat. The following are the main reasons that inspired nanotubes application in the construction of an experimental catalytic converter:

- physical and chemical properties of carbon nanotubes, as it can be assumed based on research conducted to date [3], nanotubes will not be destroyed at oxidizing conditions in a catalytic reactor,
- the large surface of carbon nanotubes layer and spatial structure that can facilitate contact with exhaust gases,
- the increased activity of the platinum in the presence of carbon nanotubes, resulting from the higher electron conductivity of carbon nanotubes and carbon nanofibers,
- related applications of carbon nanotubes in chemical reactors and filters are extensively described in the literature [3]. A special role is played by the study of catalytic fuel cells, in which platinum is combined with carbon nanotubes. The authors of many publications claim that the use of CNT and CNF may cause an increase in the catalytic activity of platinum used in the construction of fuel cells [20]

The carbon nanotubes were placed on standard ceramic carrier and coated with platinum. In subsequent versions of the reactors, the application technology of platinum on carbon nanotubes were modified, but always the total mass of platinum was several orders of magnitude smaller than in the standard reactor. It is assumed that due to high surface area of platinum in contact with the exhaust gas and electrochemical properties of carbon nanotubes it will drastically be possible to reduce the mass of platinum while maintaining a satisfactory efficacy of the reactor.

6. The study of experimental reactor surface structure

In Fig. 5, images of experimental catalytic converter are presented.

An example of the image obtained using a high-resolution transmission electron microscope (HRTEM) is shown in Fig. 6. The resulting image presents single-walled carbon nanotubes on the surface of the catalytic reactor; nanotubes are covered with platinum nanoparticles with a diameter of about 5 nm. The presence of platinum was confirmed by spectroscopic studies, the result of this study is presented graphically in Fig. 7.

7. Summary

Reasonable and probable assumption is that in the next few years reciprocating internal combustion engines will remain the dominant type of power source for cars. Nowadays there is a tendency to increase the unit power of the engines. The idea of downsizing will be developed in the future. The greater the engine boost the greater is the benefits in terms of fuel consumption. Future expectations for internal combustion engines will thus require changes in their design, for example materials that will permit to increase the thermal and mechanical loads. Nanotechnology is considered a key area of engineering activities in the twenty first century, and therefore it is reasonable to expect that it will be also used in the design of internal combustion engines in the future.

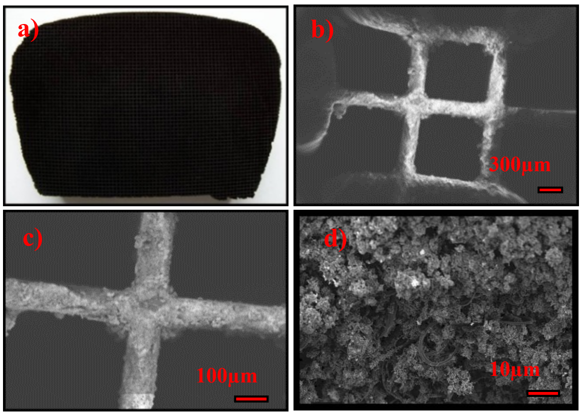

Fig. 5. Experimental catalytic reactor carrier ready to be fitted in the engine exhaust; a) the macroscopic image, b, c, d) Images recorded using a transmission electron microscope LEO 922A [21]

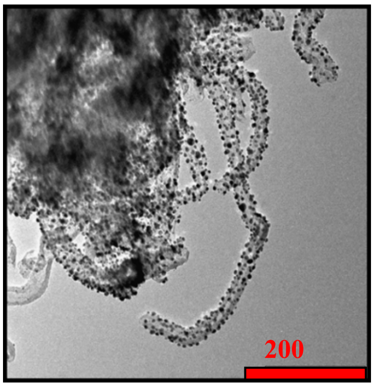

Fig. 6. The images obtained by HRTEM, showing single nanotubes on the surface of the reactor; on the surface of the nanotubes platinum nanoparticles are visible

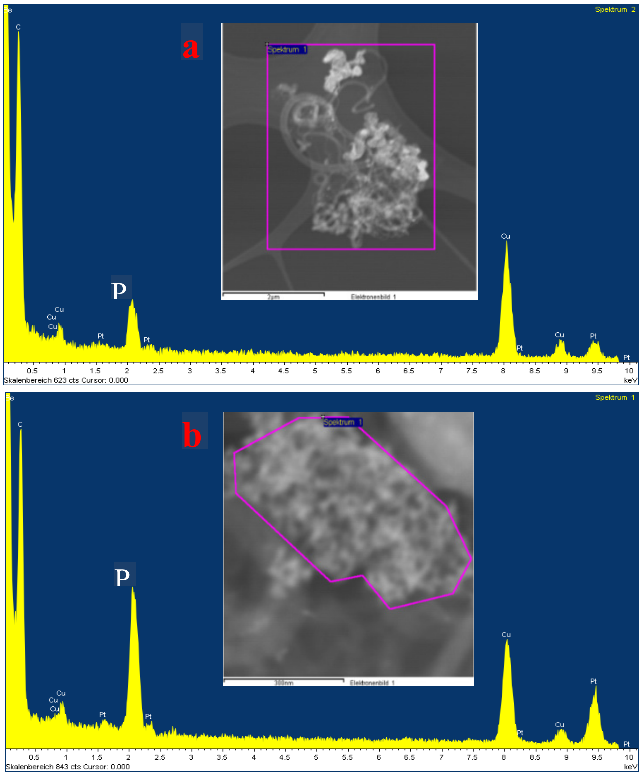

Fig. 7. The surface composition study − X-ray spectrum of areas presented in the pictures (EDX); a) sample with a side length of about 3 microns, b) irregular surface area selected from photo (a) [21]

An example of a relatively recently discovered and nowadays intensively tested nanomaterial is the carbon nanotube. Some properties of carbon nanotubes justify the attempt to their use in the construction of the internal combustion engine elements. In particular, favourable results were obtained for the experimental oxidation reactors and pistons. Improving the operation of these components requires an understanding of the phenomena occurring in the layers of carbon nanotubes, for this purpose it is necessary to carry out tests using the methods in the field of atomic physics.

The article indicates the usefulness of electron microscopy used to illustrate the structures of the surface layer of carbon nanotubes covering structural elements of the engine. The use of the scanning and transmission microscopes of a sufficiently large resolution allows to observe individual nanotubes, and in this way it is possible to determine the carbon nanotubes resistance to operating conditions in the combustion engine. The paper also presents research problems, the explanation of which requires additional research. These include primarily profile characteristic X-ray and Raman spectroscopy for some applications. Such studies offer insight into the chemical composition of the surface. This is essential for understanding the chemical reactions occurring on the surface of the reactor in the aftertreatment system and the processes of friction and wear on the piston-bearing surface.

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