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Simulation of the Exhaust Gas Neutralization Process in the Engine Combustion Chamber Using a Ceramic Coating

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Abstract

This article presents a hypothesis, phenomenological and mathematical models of the exhaust gas neutralization process of an internal combustion engine inside the combustion chamber. The neutralization of exhaust gasses is estimated from surface catalytic properties of the coating, formed on the surface of the combustion chamber parts by microarc oxidation. Phenomenological and mathematical models of the exhaust gases neutralization process in the combustion chamber were developed. Phenomenological model of neutralization process is based on particle diffusion into the surface layer of the coating. Mathematical model is based on Fick's first law and takes into consideration great amount of factors, which affect the process of neutralization: geometrical dimensions and operating characteristics of the engine; properties of coating and exhaust gasses composition. Verification of developed mathematical model was shown in this work. During verification, experimental data, acquired using motor tests of two-stroke 2-cylinder engine RMZ-551 was applied. Calculations were done for the most indicative operating mode of the engine, in which the highest effect of neutralization can be observed. A comparative analysis of the calculated and experimental data was carried out using the concentrations of the CO and NOx components. Calculated values, acquired with the developed mathematical model, differ from experimental values of concentration decrease of previously said exhaust gasses components by 23.3 and 30.4%, respectively. It shows that presented mathematical model could be used for obtaining computational high convergence results.

Keywords: Exhaust gas; internal combustion engine; microarc oxidation; diffusion; mathematical model.

1. Introduction

Active worldwide development of vehicles and energetics is tightly connected to the internal combustion engines (ICE). The amount of auto transport with ICE is increasing every year. The biggest downside of ICE is their toxicity. With working engine, following components are emitted onto the environment: CO_2 – carbon dioxide, H_2O – water, CO – carbon monoxide, C_xH_y – unburned hydrocarbons, NO_x – nitrogen oxides [1-3]. Apart from carbon dioxide and water, other exhaust gas components (EG) are byproducts of partial fuel combustion, that are toxic for a human and environment both [4,5]. Because of that, the problem of lowering EG toxicity becomes more topical at present time. To resolve this problem, Euro standards, regulating the EG toxicity of car's ICE, were developed and applied [6,7].

The Euro standards were developed by the Economic Commission for Europe and applied in the European Union countries to reduce air pollution by improving the environmental performance of car's [8-10]. The Euro standards regulate the maximum emissions into the atmosphere of the most toxic substances: carbon monoxide (CO), non-methane hydrocarbons, total hydrocarbons (C_xH_y), nitrogen oxides (NO_x), particulate matter (PM), carbon dioxide (CO_2), as well as crankcase gas emissions and fuel vapors [10-12]. Euro standards are periodically updated and tightened to encourage the development and production of more environmentally friendly car's ICE. Each subsequent Euro standard sets stricter limits on emissions of toxic substances. The Euro-6 standard was introduced in 2014 and is currently relevant. A stricter Euro-7 standard is planned to be introduced in 2027 [13-15]. But, it appeared practically harder to achieve the execution of Euro standards. It was required to improve the fuel quality and introduce special solutions into the design of engines [16,17].

There are several ways to reduce the toxicity of ICE exhaust gases [18, 19]:

- modernization of the ICE design;
- introduction of exhaust gas recirculation systems;
- improvement of engine control systems;
- use of alternative fuels and improvement of the petroleum fuels quality;
- development and integration of technologies for in-cylinder and after-treatment of exhaust gases (catalytic converters).

1. Modernization of the engine design is aimed at reducing the fuel consumer and increasing the fuel efficiency. The effect is achieved by improving the fuel spraying and perfecting the injection system. The introduction of the gasoline direct injection (GDI) and the high-pressure injection of diesel fuel reduces exhaust emissions in ICE [20, 21].

2. Exhaust gas recirculation (EGR) reduces the amount of NO_x. A small amount of EG re-enters the engine inlet manifold and mixes with the air and fuel mixture. EGR causes a decrease in the combustion temperature and suppresses the formation of nitrogen oxides (NO_x) [22-24].

3. Modern ICE control systems monitor the fuel composition and air mixture, fuel injection time and other

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engine operating parameters. Such systems help to optimize the combustion process and reduce the toxic substances amount in the EG [25-27].

4. Environmentally friendly fuels are hydrogen, biodiesel, natural gas and alcohols. Such fuels are produced from natural renewable raw materials. These fuels do not contain sulfur and their chemical composition ensures greater combustion efficiency. As a result, emissions of toxic substances in EG are reduced [28]. Purification of traditional petroleum fuels from pitch and sulfur also reduces the engines toxicity [29].

5. Provision of ecological requirements for car technology at present time is unachievable without catalytic neutralizators, that, with an assistance of oxidation reaction accelerators, are implement the EG refinement from toxic products of partial fuel combustion and oil fumes using afterburning [30]. A catalytic converter is a device that is installed in the engine exhaust system. The housing of the catalytic converter is usually made of sheet steel. A ceramic aluminum oxide substrate is located in this housing. The ceramic block has a porous structure with many cells that increase the contact area of exhaust gases with the working surface of the neutralizer. A catalytic layer consisting of platinum, palladium and rhodium is deposited on the surface of these cells. The noble metal catalytic layer converts toxic substances such as nitrogen oxides (NO_x), hydrocarbons (C_xH_y), and carbon monoxide (CO) into less toxic compounds [31-33]. Large size, complexity of construction and high cost are the main disadvantages of catalytic converters of exhaust gases. The efficiency of modern catalytic converters depends on the type of toxic gases and is up to 98%. But, the potential of catalytic neutralizators is almost exhausted nowadays.

There are several factors that do not allow to increase the efficiency of catalytic converters. The catalytic converter works effectively only in a certain range of exhaust gas composition. The converter efficiency decreases if the gas composition goes beyond this range [34, 35]. Temperature is also an important factor in the efficiency of the catalytic converter. The efficiency of the converter is reduced if its temperature is too low. If the converter temperature is too high, some parts of the converter may be destroyed. It is impossible to create a catalytic converter with maximum efficiency for different gas composition and for any temperature [35]. The effectiveness of catalytic converters depends on their design and dimensions, which must be optimized for a particular engine and car. A slight change in size or design may reduce its performance. The fuel quality also greatly affects the performance of the catalytic converter. Fuels with high levels of sulfur (S), lead (Pb) and other additives can adversely affect converter performance and increase its wear. Exhaust gas catalysts are usually noble metals. However, these metals are quite expensive and their resource is limited [36]. All of these shortcomings of catalytic converters stimulate research and development of converters alternative types. Modern converters should be made of cheap metals (copper, nickel) or oxides of copper (CuO), cerium (CeO_2), zirconium (ZrO_2) and aluminum oxide (Al_2O_3) [36].

For EG refinement effectiveness increase, lately, the possibility of partial EG toxicity decrease inside the ICE cylinder is considered. It is possible by applying special coatings for spark plugs or surfaces of combustion chamber (CC) parts [37-39].

The hypothesis about the possibility of a partial reduction in the toxicity of ICE exhaust gas due to the ceramic coating on the parts of the combustion chamber is presented in this article. The coating is formed by microarc oxidation method (MAO). The MAO-method forms ceramic porous coatings on detail surfaces from aluminum alloys. Such coatings consist of high temperature aluminum oxides: α-Al_2O_3, γ-Al_2O_3, mullit, sillimanite [40]. The hypothesis is based on next thesis:

1. MAO-coatings are composed of α-Al_2O_3, γ-Al_2O_3, aluminumsilicates (mullit, sillimanite, etc.) [41, 42]. Those substances are usually used as catalyst and his carrier [43]. Catalytic converters usually have a ceramic base of aluminum oxides and silicon oxides. Thus, MAO-coatings have the composition necessary for a catalytic converter.

2. The structure MAO-coatings differs by high porosity. The porosity value goes up to 30% [41, 42]. Large surface porosity is integral property of catalyst [44, 45].

3. MAO-coating is ceramic and has a low thermal conductivity [41]. That means that surface temperature of MAO-coating, while the engine is running, will be higher, than on metallic detail surface without coating. High temperature activates the catalysis process [46].

4. Many researchers point to the EG toxicity decreasing, while the MAO-coating for piston thermal protection or decreasing CC ICE details wearing is applied [47]. Parsadanov et al. [48] have shown that the MAO-coating of the piston crown reduces the amount of particulate emissions in the exhaust gases of a diesel engine by an average of 19%. Sakulin et al. [47, 49] found a decrease in the content of toxic components CO, CO_2 and NO_x in the exhaust gas when they investigated the heat-protective properties of the MAO coating on the piston crown of a two-stroke ICE. Osipov et al. [50] simulated the operation of ICE in a flow reactor. The MAO coating was applied to the surface of the reactor part. A decrease in the amount of carbon monoxide (CO) by 2.0-4.5% was recorded as a result of passing gas through this reactor. Lehmann et al. [51] analyzed the catalytic properties of the MAO coating and concluded that this coating can replace noble metals (Pt, Pd and Rh) in converters.

MAO coatings have a complex of positive properties: high microhardness, heat resistance, corrosion resistance [40]. MAO coatings on CC ICE parts can increase the reliability of parts, reduce the wear of surfaces and increase the surfaces resistance to high temperature [42]. The catalytic properties of the MAO coating can reduce the amount of toxic components in the ICE exhaust gas directly inside the engine cylinder.

However, the analysis of scientific literature shows, that at the present moment there are no theoretically explained researches, that confirm the possibility of using MAO-coating on CC ICE parts as a catalyst. That's why the aim of this article is theoretical explanation, development and verification of the mathematical model of EG neutralization process using MAO-coating on CC ICE parts.

2. Simulation

A. Phenomenological model of neutralization process

Phenomenological model of EG ICE neutralization with MAO-coating can be represented as a process that consists of several stages:

1. ***Gas molecule diffusion to the part surface*** (Fig. 1). The burning process of fuel-air mixture starts closely to spark plug. Exhaust gasses also appear closely to spark plug and distributes in volume of CC. As a result, the EG molecule concentration in a center of CC becomes high, and the molecule concentration at the near-wall layer will be low. The difference in concertation contributes to the molecule diffusion to the walls of CC details. High temperature, pressure and turbulization of mixture contributes to the increase in EG

molecule diffusion rate to the near-wall area. The diffusion rate depends on environmental density and viscosity, temperature, nature of diffused particles, the effect of external forces, etc. The patterns of those processes are usually described with Fick's laws [52].

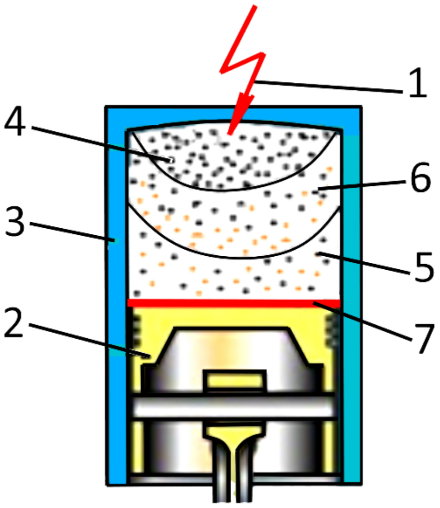


Fig. 1. Process of diffusion of EG molecules from center of CC to the surface of details: *1* – spark plug; *2* – piston; *3* – sleeve; *4* – area of high EG concentration; *5* – area of low EG concentration; *6* – transitional area; *7* – MAO-coating

2. ***Adsorption of gas molecules on part surface.*** After that, as EG molecules diffuse to the wall, their adsorption on the detail surfaces happens. As is known [53], the force fields on the surface are not balanced. Uncompensated force field has an excess energy and adsorb gas molecules on the surface after contacting with them for a period of time. Some molecules leave the surface (desorption phenomenon). Their place is taken by newer ones. The balance is established at which the adsorption rate is equal to the desorption rate. The universal scheme of this process is shown in Fig. 2a. Adsorption is an exothermic process, similar to many other processes of forming new connections. That is why increase in temperature strengthens the desorption, and increase in pressure strengthens the adsorption.

3. ***Diffusion of EG molecules deep inside coating.*** The neutralization process is described with an account of presence of MAO-coating on the detail surface. This coating has a high porosity - up to 30 % [41, 42]. The diffusion of some EG particles occurs deeply inside the pores and cracks (Fig. 2b.). High temperature on the surface will contribute to the diffusion of EG molecules inside the surface.

4. ***Chemical reaction of neutralization.*** The process of neutralization is that the engine EG components (CO, NO_x, C_xH_y) and surface of the catalyst (Al_2O_3 and aluminumsilicates), exchange in active atoms, which leads to the neutralization of gasses. As a result, new substances appear (CO_2, N_2, H_2O).

Oxygen molecules are adsorbed on the catalyst surface (Fig. 3a). As a result, connections «catalyst-oxygen» are formed. Connections between oxygen atoms are weakening. When toxic substance molecules (CO, NO_x, C_xH_y) are getting closer to the adsorbed oxygen (Fig. 3b), new chemical connections and substances appear. Taking into account the catalyst in the form of MAO-coating, the classical neutralization equations have the next form:

$$2CO + O_2 \xrightarrow{t, Al_2O_3} 2CO_2,$$

$$NO_2 + O_2 \xrightarrow{t, Al_2O_3} N_2 + O_2,$$

$$NO_2 + O_2 \xrightarrow{t, SiO_2} N_2 + O_2,$$

$$C_xO_y + O_2 \xrightarrow{t, Al_2O_3} xCO_2 + \frac{y}{2}H_2O,$$

$$C_xO_y + O_2 \xrightarrow{t, SiO_2} xCO_2 + \frac{y}{2}H_2O.$$

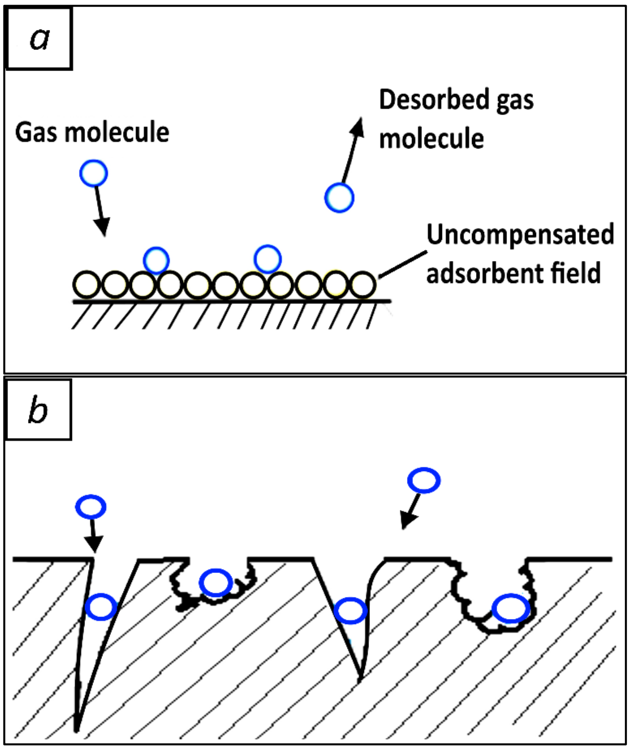
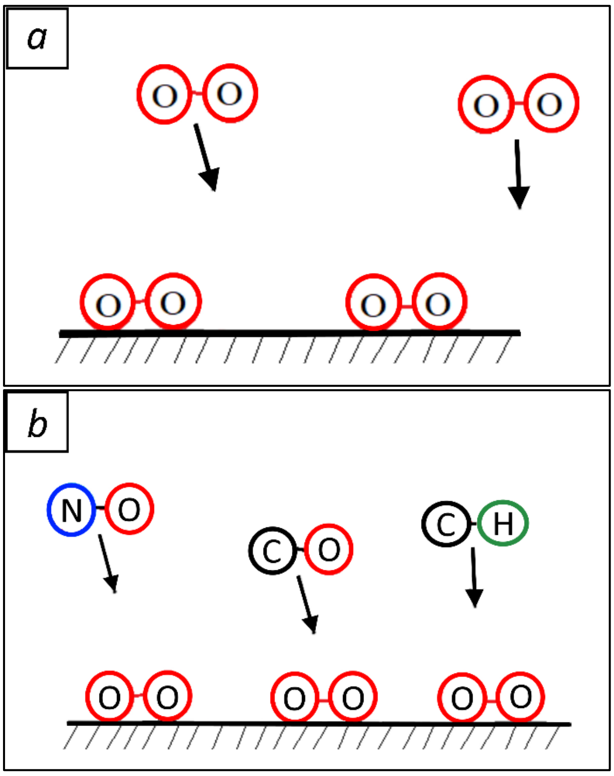


Fig. 2. Adsorption and diffusion of gas molecules on the surface: *a* – adsorption of gas molecules on the surface; *b* – diffusion of gas molecules inside the pores and cracks in the surface



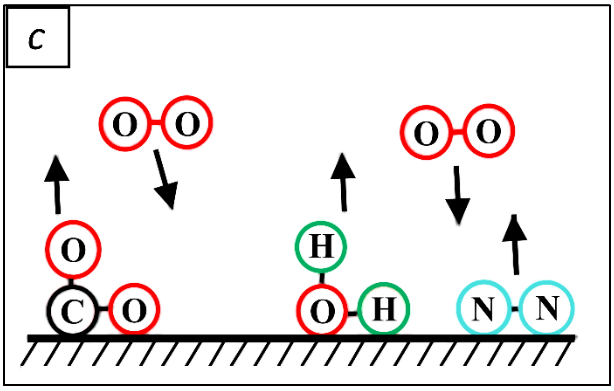


Fig. 3. Scheme of process of EG neutralization on the surface of MAO-coating: *a* – diffusion and adsorption of oxygen molecules on the surface; *b* – diffusion and adsorption of CO, C_nH_m and NO_x molecules on the surface; c – reaction of neutralization and desorption of CO_2, N_2 and H_2O molecules

5. ***Desorption of molecules (products of reaction) from the surface.*** The next stage after neutralization is the desorption of molecules (reaction products) from the coating surface (Fig. 3c). The same way will the process in coating's pores happen.

It is known, that rate of chemical reaction is limited by the slowest stage of this process. The analysis of literature shows, that for zeolite catalyst, the limiting stage is a process of molecule diffusion in the pores of the catalyst [54]. That is why the mathematical model of a process, shown in the next chapter, based on said thesis.

B. Mathematical model of exhaust gasses neutralization process in ICE

Mathematical model of EG neutralization in CC by MAO-coating should account to the mass of factors: geometrical dimensions of CC ICE; properties of MAO-coating; properties and composition of EG; engine operating parameters. Complex of these factors was taken into account in the developed mathematical model (Fig. 4).

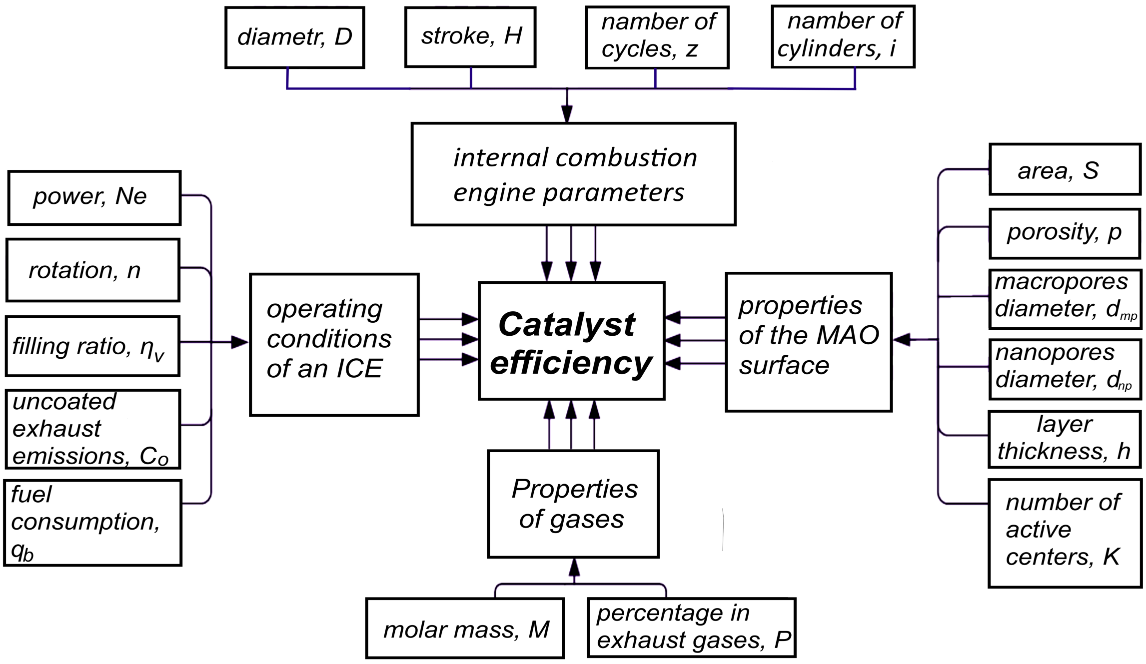


Fig. 4. Factors effecting the chemical reaction of neutralization

Fick's first law was taken as the base for mathematical model. According to this law, the amount of substance A transferred by diffusion per unit time through the surface S, perpendicular to the direction of transfer, is proportional to the concentration gradient of this substance at that moment of time *t* [52]:

$$dq = -D\cdot S\cdot\left(\frac{\partial C}{\partial x}\right)\cdot\partial t, \tag{1}$$

where dq – quantity of substance, mg; C – concentration of reacting substances (CO, NO_x, C_xH_y), mg/m^3; t – exhaust gas contact time with MAO-coating, s; D – diffusion coefficient, m^2/s; x – rectangular coordinates, m; S – area of contact of EG with MAO-coating, m^2.

General EG concentration decrease will be found using Eq. 2:

$$dC = \frac{dq}{Q_{EG}}, \tag{2}$$

where Q_{EG} – medium EG volume per second, m^3/s.

Mathematical model was developed based on equations (1) and (2), and also based on known equations, that describe the working ICE.

The volume of exhaust gas is determined by the Eq. 3 [25]:

$$Q_{EG} = \frac{\gamma\cdot Q_A + \frac{q_b\cdot N_b}{3600}}{\gamma}, \tag{3}$$

where γ – specific air density, kg/m^3; Q_A – volume air-quantity flow, m^3/s; q_b – specific effective fuel consumption, kg/(kW·h); N_b – efficient engine power, kW.

The volume air-quantity flow Q_A is determined by the Eq. 4 [55]:

$$Q_A = \frac{\pi D^2\cdot H\cdot i\cdot n}{120\cdot z}\cdot\eta_V, \tag{4}$$

where D – cylinder diameter, m; H – piston step, m; i – number of cylinders; n – speed of rotation of the crankshaft, min^{-1}; z – number of cycles; η_v – charge volume-to-chamber volume ratio.

The MAO coating has macropores and nanopores in its structure. The diameter of the macropores and the diameter of the nanopores were taken into account when compiling the final mathematical model. The diffusion coefficient was determined by the Eq. 5 for a porous material:

$$D = \frac{1}{3}\sqrt{\frac{8RT}{\pi \cdot M_i}} \cdot (d_{mp} \cdot P_{mp} + d_{np} \cdot P_{np}), \qquad (5)$$

where M_i – the molecular weight of the exhaust gas i-component; R – universal gas constant, d_{mp} – the diameter of coating macropores, m; d_{np} – the diameter of coating nanopores, m; P_{mp} – macroporosity of the coating, fractions; P_{np} – nanoporosity of the coating, fractions.

The concentration gradient was considered as a gas gradient in the coating pore. It was assumed that the concentration of the gas component varies with the coating thickness from the concentration value in CC to zero in the pores. (Eq. (6)):

$$\frac{\Delta C}{\Delta x} = \frac{C_o}{h}, \qquad (6)$$

where C_o is the concentration of the exhaust gas component in the combustion chamber; h – coating thickness.

The final mathematical model takes into account the Eq. (1), (2), (3), (4), (5) and (6):

$$\Delta C = \left(\frac{1}{3}\sqrt{\frac{8RT}{\pi \cdot M_i}} \cdot (d_{mp} \cdot P_{mp} + d_{np} \cdot P_{np}) S_0 \cdot i \cdot L^2 \cdot K \cdot \frac{C_{0i}}{h} \cdot t\right)/Q_{EG}, \qquad (7)$$

where R – universal gas constant, J/(mol·K); T – piston surface temperature, K; M_i – molecular mass of i number of components, kg/mol; S_0 – the surface area of the MAO coating in one cylinder, m^2; i – number of engine cylinders; L – coefficient accounting for roughness of surface; K – share of active catalyst centers; C_{oi} – concentration of EG components in CC; h – thickness of coating, m; t – contact time EG with the MAO coating, s; Q_{EG} – the volume of exhaust gases according to Eq. (3) and (4), m^3/s.

The empirical coefficients K and L were introduced into Eq. (7). Chemical catalysis reactions occur at the active centers of the surface. The coefficient K takes into account the number of active centers on the coating surface. The roughness and undulation of the surface increase the actual surface area. The coefficient L takes into account this effect and is determined experimentally.

3. Results and Discussion

Developed mathematical model was realized for piston ICE RMZ-551. The data on EG toxicity and fuel consumption obtained during the tests described in [49] were used to calculate and verify the mathematical model.

The engine RMZ-551 is a two-stroke 2-cylinder with liquid cooling. The engine power is 36.78 kW with nominal rotating frequency of 6250 min^{-1}. Cylinder diameter is 72 mm, piston stroke is 61 mm. This engine is used on snowmobiles.

Data on EG toxicity, obtained from motor tests of base engine and engine which pistons were coated with MAO, is shown in article [49]. Engine tests were carried out with covered pistons and uncovered pistons. The purpose of the tests described in the article [49] was to reduce the burnout of pistons. However, the authors of the work recorded a decrease in the toxicity of exhaust gases in some engine operating modes. Verification of the developed model was carried out on the basis of these experimental data.

The coating was applied only to the bottom of pistons for thermal protection. The bottom area is 4071.5 mm^2. The macroporosity of the coating was calculated and is equal to 28.7%. Thickness of coating is 120 μm. Temperature on the bottom of piston with MAO-coating was taken as 695 K [56]. The data were taken for calculations from the article [56], in which the simulation of piston thermal state of said engine with MAO-coating bottom coating was carried out. Preliminary estimation of MAO-coating has shown, that the coefficient accounting for roughness of surface can be taken as $L = 2.36$. In calculations it was also taken, that share of active centers in catalyst $K = 0.04$, as for zeolite catalysts [57, 58]. The calculations assumed that the contact time of EG with the MAO coating is half of the engine cycle. This value per second of engine operation is 0.5 sec ($t = 0.5$ s). The specific air density $\gamma = 1.293$ kg/m^3 was taken into account in the calculations. The charge volume-to-chamber volume ratio was $\eta_v = 0.85$ [55].

Comparison of experimental and calculated data was carried out for one engine mode. Mathematical model (Eq. 7) was used for calculating the value of decrease of EG components toxicity at the operating mode: 6000 min^{-1} and 10 % throttle opening. The choice of operating mode was justified, because the highest effect of decreasing EG toxicity was fixated exactly on that mode. The concentration of CO was 27073.9 mg/m^3 (2.33%) and NO was 5.97 mg/m^3 (4.8 ppm) in an engine with an uncovered piston. The concentration of CO was 9295.7mg/m^3 (0.8%) and NO was 3.73 mg/m^3 (3 ppm) in an engine with a coated piston. The results of comparison between experimental and calculated data in the Tab.1.

Table 1. Experimental and calculated data of decreasing EG toxicity of experimental engine

Exhaust gasses components	**Reducing the concentration of exhaust gasses components, mg/m³**		
	Experiment	***Simulation***	***Error, %***
CO	17 778.15	21 922.95	23.3
NOx	2.24	2.92	30.4

The calculation results and experimental data show that the MAO-coating on the piston bottom reduces the concentration of engine exhaust gases. The analysis of Tab.1 shows that the difference between the experimental and calculated values is insignificant: for carbon monoxide, CO is 23.3%, and for nitrogen oxide, NO_x is 30.4%. The difference between the calculated and experimental data is due to the fact that the mathematical model contains empirical coefficients and some variable values that were determined from the scientific literature or as a result of studying samples.

4. Conclusions

This paper presents a substantiated hypothesis about the possibility of reducing the toxicity of ICE exhaust gas with the help of an MAO-coating formed on the surfaces of CC parts. Phenomenological and mathematical models, describing the decrease of concentration of EG components for piston ICE were developed. Mathematical model was based on Fick's first law and accounts for mass of factors: geometrical dimensions engine and CC ICE parameters; properties and structure of MAO-coating; properties and composition of EG; operating engine parameters.

During the study, mathematical model for calculating indicators of EG toxicity of RMZ-551 engine was used. To verify the mathematical model, the experimental data of motor tests of the indicated engine were used. Comparison of calculated and experimental data has shown a small difference of 23.3% in CO and 30.4% in NO_x. The presented mathematical model can predict the exhaust gases composition of ICE with MAO coatings on the details of the combustion chamber.

The research results can be used in the development and design of reciprocating ICE to reduce their toxicity.

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