

# APPLICATION OF THERMAL BARRIER COATINGS FOR INTERNAL COMBUSTION ENGINES (Review)

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Literature data on application of thermal barrier coatings for protection of internal combustion engine components have been generalized. The methods used to apply thermal barrier coatings and materials used to deposit them are considered.

**Keywords:** thermal barrier coatings, internal combustion engines, parts of piston-cylinder group, plasma spraying, partially stabilized zirconium dioxide

At present the main kind of engines used in the drives of automotive, ship and railway transportation, agricultural machinery and quite a number of other machines and units are internal combustion engines (ICE) [1].

The main causes for lowering and loss of ICE serviceability are abrasive wear in friction pairs (piston rings and sleeves, crankshaft slide bearings, distribution shaft cams, etc.), cavitation wear (cylinder sleeves) and corrosion-mechanical wear (valve disc and seat) [1]. In addition, quite important is effective insulation of the combustion chamber with thermal-barrier coating (TBC) which enables redistribution of dissipated heat in such a way as to minimize its losses through the cooling system and exhaust gas removal system. Piston corrosion is caused by vanadium oxide and sulphide precipitates that are highly aggressive at temperatures of the surface of combustion chamber parts (400–500 °C). Improvement of antifriction properties of the parts allows lowering friction losses, which in the above components are equal to 50 % of total mechanical losses in the engine, and, thus, increasing the cost-effectiveness of its operation. The most promising method to lower the temperature of ICE parts, improve wear resistance of friction pairs, and protection from corrosion, is development of thermal barrier, wear- and corrosion-resistant coatings on part surface. Figure 1 shows car parts with TBC.

SULZER METCO is the best known abroad company involved in development and sale of equipment and manufacturing of consumable materials for deposition of various-purpose coatings. Given below is the information on coating materials most often applied for coatings used for repair of automotive parts. At repair of braking system parts (brake discs, brake blocks) plasma coatings from  $\text{Al}_2\text{O}_3\text{-}3\text{TiO}_2$ ,  $\text{Ni}_5\text{Mo}_5.5\text{Al}$  and molybdenum powders are used to improve the braking process, lower the weight, and extend the service life of discs and blocks. For engine system parts exposed to wear in service (piston rings, diesel injector, distribution shaft, crankshaft) plasma coatings from molybdenum and  $\text{Mo-NiCrBSi}$  powders, flame coatings from  $\text{Fe}_{38}\text{Ni}_{10}\text{Al}$  and  $\text{Fe}_{13}\text{Cr}$  wires, coatings applied by arc metallizing from  $(\text{WC-}12\text{Co})_{38.8}\text{Ni}_6\text{Cr}$  wire and coatings applied by supersonic flame spraying from  $\text{Cr}_3\text{C}_2$  and  $\text{Cr}_3\text{C}_2\text{-NiCr}$  powders are used, which ensure high jamming resistance, high wear resistance, reduced friction, saving on costs, and extension of component service life. At corrosion (valve stem, exhaust sensor) plasma coatings from spinel powders and coatings from aluminium wire spray-deposited by arc metallizing are applied, which extend the valve life and ensure oxygen control. At oxidation (oxygen sensors) plasma coatings from ceramic powders and at high temperatures (piston top) – plasma coatings from  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  powders are applied for erosion protection, which ensure lowering of surface erosion and heat losses, thermal insulation, increase of engine operation effectiveness, and extension of piston operation term. To avoid weight increase because of heavy cast iron inserts,

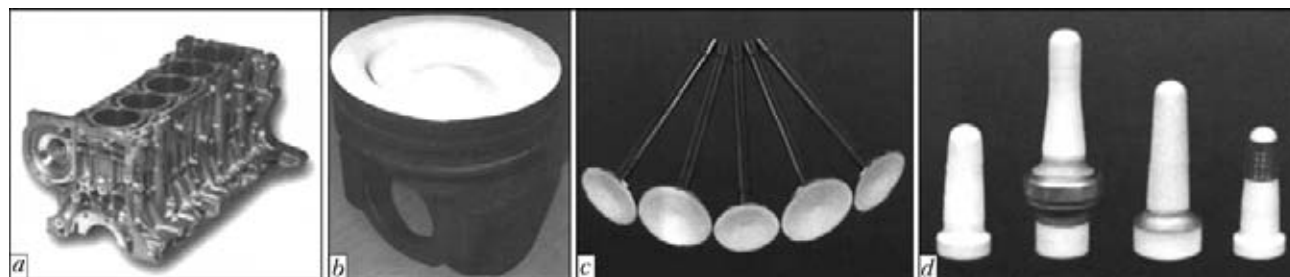


Figure 1. ICE parts with TBC: a – engine cylinders; b – piston; c – exhaust valves; d – exhaust sensor, oxygen sensor

plasma coatings from Mo, MoFe, Fe and other powders are applied on engine cylinders, which reduce engine dimensions and oil and fuel consumption. In case of an adhesion problem on the interface between the cylinder sleeve and cast aluminium block of the cylinder, coatings from AlSi wire, spray-deposited by arc metallizing and flame coatings from NiAl wire are applied, which improve the surface of aluminium casting and its functionality. In case of dielectric insulation (generator cover), plasma coatings from Al<sub>2</sub>O<sub>3</sub> powders are used. For exhaust system components at increased heat radiation and higher temperature of exhaust gases plasma coatings from ceramic powders, flame coatings from aluminium wire for thermal insulation, thermal shielding, temperature lowering, and saving on costs are applied, and flame coatings from aluminium wire are applied under corrosion conditions on exhaust muffler to achieve a longer service life at low cost.

The main direction of increasing ICE power is raising the temperature and degree of working gas compression at fuel combustion [2]. Therefore, the problem of increasing working temperature in the combustion chamber due to lowering of heat losses in the cooling system is becoming urgent. The most promising method to solve this problem is application of TBC, at deposition of which engine operation mode is optimized, their efficiency is increased, and consumption of fuel and lubrication materials is reduced.

Development of TBCs for propulsion engineering is given a lot of attention in the USA, Japan, Great Britain, Germany and Norway. In CIS countries (Russia, Ukraine, and Belarus Republic) research is conducted on development of various coatings (including TBCs) to improve ICE effectiveness and reliability. At present, TBCs have found wide application in Ukraine for protection of blades of gas turbine engines (GTE) [3], while development of TBCs for ICE components is practically absent.

The main purpose of TBCs in ICE is lowering of heat losses in the combustion chamber and protection of the metal base from high temperature impact. As a rule, TBC consists of an insulating outer ceramic layer (upper) and metal layer (bond coat) between ceramics and base (Figure 2) [4, 5]. Thermal barrier

functions are fulfilled by outer ceramic layer. The main function of the bond coat is plastic relaxation of stresses in the coating, arising because of uncoordinated change of the volumes of ceramic and metallic materials at item heating and cooling.

Ceramic materials mainly used for TBCs are zirconium dioxide, partially stabilized by oxides (7–8 % Y<sub>2</sub>O<sub>3</sub>, 22 % MgO, 25 % MgO, 5 % CaO), aluminium oxide, and chromium oxide [5, 6]. Zirconium oxide partially stabilized by yttrium oxide became the most widely accepted [4, 5]. Wide application of ZrO<sub>2</sub> is due to its low coefficient of heat conductivity (1.95 W·m<sup>-1</sup>·K<sup>-1</sup>), high coefficient of linear expansion ( $\alpha = (5.0-5.6) \cdot 10^{-6} \text{ K}^{-1}$ ), high-temperature strength and high fracture toughness.

Used as bond coat material are high-temperature resistant alloys based on MeCrAlY (Me = Ni, Co, Ni-Co, Fe), as well as NiCr. The most widely accepted for this purpose is NiCrAlY that is due to its high oxidation resistance (up to 900–1000 °C) and good ability to relax stresses in the coating.

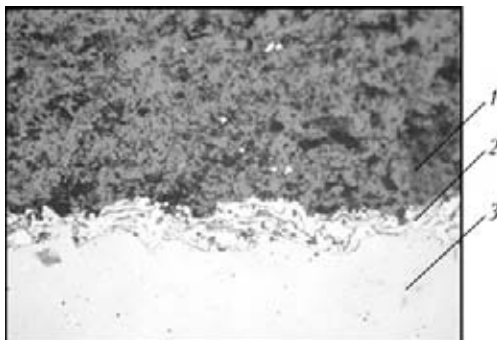
Such spraying methods as plasma method (in open air [1, 2, 4, 5, 7–13], at low pressure or in inert-gas atmosphere [5, 8]) are used for deposition of functional protective coatings.

The main method for deposition of TBC ceramic layer is plasma spraying in air (up to 90 % of developments) [5]. Predominant acceptance of plasma spraying of TBCs is due to its high efficiency and versatility that allows application of metal and ceramic materials of specified chemical and phase composition in the form of coatings of a considerable thickness.

High-temperature bond coat is deposited by the methods of plasma spraying in inert atmosphere or dynamic vacuum, and electron beam vacuum deposition to prevent bond coat material oxidation during spraying.

Up to now most of the developments on coatings of ICE parts falls to the share of piston group (more than 90 %, including piston rings at about 70 %) [2, 5, 7, 8, 10–13].

It is established [2] that one of the important factors of service properties of coatings from ZrO<sub>2</sub> is the spray-deposited layer thickness. Coatings from ZrO<sub>2</sub> 0.1–0.5 mm thick on cast iron piston rings lower the temperature of piston «hot» points by 45–50, piston top temperature — by 25, and in the region of upper piston ring — by 10 °C, have an equalizing impact on piston head temperature field, that promotes lowering of thermal stresses, which are the causes for cracking in cast iron pistons. Effectiveness of coating application is the greater, the higher the piston temperature at operation without the coating. After 9490 h of operation ZrO<sub>2</sub> coatings of the above thicknesses (0.1–0.5 mm) did not have any spallations, and after 12,854 h of operation small spallations appeared on the top edge, and coatings continued operating up



**Figure 2.** Microstructure (×200) of two-layer TBC: 1 — ceramic layer; 2 — metal bond coat; 3 — base

to 22,548 h (6 years of operation) [2]. At deposition of  $ZrO_2$  coating on a steel piston, heat transfer in the cooling system decreased by 26 % that allowed, in an engine with lower heat removal, reducing radiator working surface by 21 % and lowering power consumption of cooling ventilator by 3 kW [8]. In [12] it is established that coating on an aluminium piston from  $ZrO_2$  1 mm thick does not have any damage of the layer after 50 h of operation, and at coating thickness of 2 mm crumbling and spallation of the ceramic layer are observed. Coating on a ship engine aluminium piston from  $ZrO_2$ , stabilized by 5 % CaO, remained intact after 3.5 years of operation, although it had a carbon layer on it [7].

Plasma coatings from  $Al_2O_3$  0.45–0.5 mm thick on a piston lower the temperature in the top center by 31, and in the piston ring area — by 12 °C.  $Al_2O_3$  TBCs on pistons showed a good performance after 500 h of operation, no fractures were observed inside the chamber, while in cast iron pistons slight spallations in TBCs on top edge developed only after 12,854 h of operation, but coatings continued to operate up to 22,548 h (6 years of operation).  $Al_2O_3$  coating more than 1 mm thick on a cast iron piston turned out to be non-serviceable, but at smaller thicknesses it operates without fractures. On aluminium pistons the serviceable thickness of this coating is not more than 0.4 mm at piston preheating before coating deposition. Without preheating of the aluminium base the above thickness is non-serviceable, because of considerable tearing and tensile residual stresses, as well as cyclic thermal stresses arising at operation in the diesel engine [2].

Two-layer coatings of the total thickness of 1 mm from stabilized  $ZrO_2$ –24 % MgO and FeCrAlY bond coat on an aluminium piston did not fail after testing for 5000 h [10]. Thermal cycling tests at the temperature from 0 up to 950 °C of two-layer coatings from  $ZrO_2$ –20 % MgO + NiCrAlY,  $ZrO_2$ –8 %  $Y_2O_3$  + NiCrAlY,  $ZrO_2$ –25 % MgO + CoNiCrAlY,  $ZrO_2$ –20 % MgO + NiCoCrAlY of less than 1 mm thickness on aluminium pistons showed that TBCs have sufficient resistance relative to cyclic temperature variations. Coating fracture occurs because of oxidation of MCrAlY bond coat. Coating from stabilized  $ZrO_2$ –7/8 %  $Y_2O_3$  showed higher resistance at the temperature above 1000 °C [9]. Two-layer coating on aluminium piston from stabilized  $ZrO_2$ –5 % CaO with 20Ni80Cr bond coat 1.5 mm thick cracks and breaks up after 50 h (2800 heating–cooling cycles) [12].

On cast iron piston two-layer coating from  $Al_2O_3$  0.6 mm thick with NiCr bond coat 0.1 mm thick provides temperature lowering in the «hottest» points of piston top in the zone of the impact of flame plume by 40–48, and in the zone of piston upper groove — by 8–10 °C. On an aluminium piston a coating from  $Al_2O_3$  with NiCr bond coat lowered the temperature by 15–20, and in the upper groove zone — by 5–7 °C [2].

Two-layer coating from stabilized  $ZrO_2$ –22 % MgO with NiCoCrAlY and NiCrAlY bond coats of approximately 0.4 mm thickness on the top of a cast iron piston remained unchanged after 500 h of testing, and coating from  $ZrO_2$ –8 %  $Y_2O_3$  with NiCoCrAlY and NiCrAlY bond coats remained intact even after 9000 h of testing [11]. Coating from  $ZrO_2$  of up to 2 mm thickness on the top of a steel piston reduces heat transfer into the cooling system by 30.4, increases effective power by 3.75, and reduces specific fuel consumption by 3.58 % [8].

On heads of pistons from high-temperature 2Kh13 steel  $Al_2O_3$  and  $ZrO_2$  coatings on NiCr bond coat of more than 0.4 mm thickness have small spallations after running for 163,332 km, and the rest of coating surface remains in good condition without cracks [2]. Two-layer coating from  $ZrO_2$ –7 %  $Y_2O_3$  with NiCrAlY bond coat on aluminium piston head reduces specific heat removal by 30 %, fuel saving being 5–10 % [13].

Coatings of cermet composition are used to lower piston temperature and heat flows through the piston [2]. Coating of cermet composition  $ZrO_2$ –Ni 0.7 mm thick with higher heat conductivity has lower heat resistance than that from  $Al_2O_3$  0.6 mm thick, so that its effectiveness is also lower. Heat resistance increases with increase of coating thickness, but not in proportion to layer thickness. Long-term testing for 917 h of cermet coating performance in the pistons showed that the coatings do not have any fractures [2].

Multilayer coatings of cermet composition with gradually changing coefficient of linear expansion have higher performance compared to purely ceramic coatings, and can be used with success on cast iron, steel and aluminium pistons. Multilayer coatings with  $ZrO_2$ –Ni ceramic surface layer 0.3–0.4 mm thick with NiCr bond coat 0.1 mm thick on aluminium pistons have operated for 397–1104 h in different modes [2].

$Al_2O_3$  coating 0.25–0.35 mm thick on cylinder sleeve withstood testing under the impact of thermal shocks without fracture, at 0.5 mm thickness it had no spallations during testing, but coating cracking under the impact of tensile stresses was observed in more heated areas [2]. Conducted thermal cycling testing of two-layer TBCs from  $ZrO_2$  stabilized by MgO,  $Y_2O_3$  and CaO oxides with CoNiCrAlY bond coat on cylinder sleeves at temperatures from 50 up to 1100 °C showed that coating from  $ZrO_2$ –7 %  $Y_2O_3$  withstood 20,000 cycles,  $ZrO_2$ –20 %  $Y_2O_3$  — 2500,  $ZrO_2$ –24 % MgO — 12,000,  $ZrO_2$ –5 % CaO — 3000 cycles, respectively. Two types of cracking — perpendicular (segmented) and parallel are found in  $ZrO_2$ –7 %  $Y_2O_3$  coating with CoNiCrAlY bond coat after thermal cycling [7].

On cylinder head  $ZrO_2$  coating 2 mm thick and two-layer coating from  $ZrO_2$ –24 % MgO with FeCrAlY bond coat do not have any traces of degradation and do not fail after testing for 5000 h [10]. When coating from  $ZrO_2$  3 mm thick on cylinder bushing is

used no crumbling or spallation of coating is observed after 50 h of operation [12].

Results of testing flat flame surface of cylinder cover with  $ZrO_2$  coatings of 0.4–0.5 mm thickness showed that the coating slightly increases the temperature of cylinder piston and busing and leads to redistribution of heat flows passing through the parts [2].

Analysis of factors determining the thermal and mechanical stress level of exhaust valves shows the rationality of TBC application on exhaust valve discs [2]. TBCs on the valves lower not only the valve temperature, but, what is most important, the temperature gradients in the valve disc and, therefore, also thermal stresses in it. With increase of TBC thickness, decrease of temperature gradients becomes smaller. Coating ensures the greatest lowering of temperature gradients of the valve disc at its deposition not on the entire diameter, but on a diameter smaller than the full diameter by the size of chamfers. In the central part of valve disc  $ZrO_2$  coating 0.5–0.6 mm thick lowers the temperature in the disk center by 60 and increases the temperature of valve edge by 15–20 °C [2].

Coating from  $ZrO_2$  on exhaust valve was covered by hairline cracks after 180 h of functioning, that lowers the thermal stresses and leads to stopping of further breaking cracking along ceramics/metal interface. Valve continued operating without any considerable damage up to appearance of corrosion at fuel contamination, which led to formation of craters and after 800 h of operation  $ZrO_2$  coating failed [7]. Testing of valves with coatings from  $ZrO_2$  stabilized by oxides — 24 % MgO and 8 %  $Y_2O_3$  — for 4000 h showed good service life of both the coatings on valve surface. Mass loss rate of ceramics as a result of erosion was higher for  $ZrO_2$  stabilized by MgO than for  $ZrO_2$  stabilized by 8 %  $Y_2O_3$ . At testing for 5000 h coatings on valves did not fail [10]. For greater lowering of temperature gradients in the valve it is rational to apply anisotropic coatings characterized by low heat conductivity in the axial direction of coating layer and greater heat conductivity along the coating layer. Such properties are characteristic for multilayer coatings consisting of alternating layers of ceramics and metal. Ceramic layers prevent passing of thermal flow from gases to valve disk, and metallic coatings transfer the heat from the center to edges of valve disk. At correct selection of composition and thickness of coating layer it is possible to achieve such a temperature field of the valve which ensures the smallest thermal stresses in it [2]. Three-layer coatings from  $ZrO_2$ –24 % MgO with NiCr and NiCrAlY bond coats 0.7 mm thick on exhaust valves lowered metal temperature by 50 °C. The smallest temperature lowering was recorded in the area of valve seat (because of circular seat water cooling) [10].

On valve sealing surfaces two-layer coatings from  $ZrO_2$ –8 %  $Y_2O_3$  with NiCoCrAlY and NiCrAlY bond

coats have localized small delamination in the upper part of ceramic coating after 500 h of testing. Coatings from  $ZrO_2$ –22 % MgO with NiCoCrAlY and NiCrAlY bond coats on valve sealing surface almost completely came off the valve surface after 500 h of testing, because of  $ZrO_2$  destabilization at running of chemical reaction between MgO and sulphur, and after 9000 h of testing valve surfaces failed, and MgO concentration in the coating dropped to 3 % [11].

Analysis of experimental results shows that TBCs on combustion chamber parts, reducing heat removal, allow them to be better used for organizing the combustion process and improving the effectiveness of the engine [2]. At testing of coatings on combustion chamber parts, researchers focused on reducing heat removal into the coolant, and thus improving the effectiveness of ICE operation. TBC from  $ZrO_2$  2.5 mm thick on combustion chamber increases engine effectiveness by approximately 7.5 %, and at 3 mm thickness heat losses through combustion chamber walls decrease by about 50 % [12]. Two-layer TBC from stabilized  $ZrO_2$ –8 %  $Y_2O_3$  with NiCrAlY bond coat 2 to 2.5 mm thick on combustion chamber decreases the amount of energy consumed in coolant heating and lowers fuel consumption by the engine to 10 g/l, and the coating can stand more than 10,000 thermal shocks [12].

Analysis of the results of studies aimed at lowering ICE piston temperature at TBC application, depending on load level, boosting, rotation frequency, diesel engine dimensions and coating properties, leads to the conclusion that it is mainly determined by heat resistance of the piston and coating. Heat resistance of the piston depends on the design, diameter and heat conductivity of the material, and heat resistance of the coating — on its thickness and heat conductivity. Heat resistance of a coated piston is influenced to a certain extent by heat conductivity of the zone of coating contact with the part surface, as well as coating roughness. Smooth surface of the coating promotes greater lowering of piston temperature that leads to improvement of its cost effectiveness. In addition to the above factors, the nature of working process running has a certain influence on lowering of piston temperature at TBC application. Coating on piston top also leads to redistribution of heat flows through cylinder cover and bushing, increases the heat flow to cylinder cover and decreases the heat flow through the bushing (except for its upper girth). Thermal protection of these components not only lowers their temperature and thermal stresses, but also reduces heat removal into the cooling system, that should positively influence the engine efficiency and lowering of weight and overall dimensions of heat exchanger devices.

The main causes for fracture in the coating are thermal stresses, caused by temperature mode in the combustion chamber, piston top design, as well as thickness and physico-mechanical properties of the ceramic coatings proper. Fracture of two-layer TBC

most often occurs in the interlayer zone, because of high compressive stresses in the coating. Fracture is also affected by perpendicular and parallel cracks in the coating. Perpendicular cracking, caused by tensile stress field, is believed to be favourable for coating fatigue life, as it relieves the stresses, allowing the coating to expand and contract, without experiencing any considerable shear stresses. Parallel cracking developing as a result of breaking shear stress leads to coating fracture.

Long-term service testing of engines with coatings on pistons revealed that coatings, lowering thermal stresses in the piston, allow increasing their reliability and service life to a considerable extent. Reducing the heat flow through the piston, the coating improves lubricating oil performance, thus preventing gumming-up of piston rings. At lowering of dynamic loads and piston temperature, the coating considerably reduces the wear of parts of cylinder-piston group. All this promotes extension of service life of the diesel engine and lubricating oil. TBCs increase the reliability and service life of pistons by not less than 1.5 times. These coatings lower the piston temperature and dynamic loads, and, hence also diesel engine noise and vibration, toxicity of their exhaust gases, wear and carbon deposits on parts of cylinder-piston group, and they also improve cost-effectiveness and lubricating oil performance, as well as reliability and service life of pistons as a whole.

On piston head TBC is also intended to ensure corrosion resistance of its material at high temperatures that reduces carbon deposition.

TBC on cylinder head increases exhaust gas temperature by approximately 30 °C and shortens the delay time of the moment of fuel ignition in the cylinder by approximately 10 %, compared to uninsulated engine.

On exhaust valves TBCs reduce the heat supply to the valve that allows maintaining the temperature on the seat surface below the threshold value of high-temperature corrosion in aggressive media.

Testing data showed that at TBC application the heat flow through the combustion chamber to the coolant can be reduced by approximately 30 %. As a result, it is possible to use a greater amount of heat from exhaust gases, for instance, for pumping. This results in higher total thermal efficiency. Higher average temperature will positively influence the combustion process and level of smoking exhaust.

TBC application on ICE parts ensures: up 11 % fuel saving; up to 20 % extension of engine life; re-

duction of exhaust toxicity for  $\text{NO}_x < 5$ ;  $\text{CO} < 15.5$ ;  $\text{HC} < 1.3$  and for sooty exhaust  $< 0.10 \text{ g}/(\text{hp}\cdot\text{h})$ , of quantity of solid particles in exhaust gases by 52 %, engine smoking by 75 %, noise characteristics by 3 dB, engine temperature by 100 °C; extension of fatigue life of exhaust valves by 30 %; and lowering of engine cost due to application of less expensive and deficit material at other conditions being equal.

Thus, TBCs on the piston and other parts of the combustion chamber essentially improve diesel engine performance. «Rigidity» of the combustion process and maximum pressure at combustion are lowered, thus reducing the noise, diesel engine vibration and toxicity of exhaust gases. Increase of combustion speed in the main arcing phase increases the combustion efficiency and ensures a more cost-effective operation.

TBC application should be determined by their purpose for each concrete diesel engine. In each case, their maximum effectiveness can be achieved by varying the coating thickness and composition.

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