INVESTIGATIONS INTO THE DEGRADATION MECHANISM OF THERMAL BARRIER APPLIED IN IC ENGINE

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Abstract

In the present paper the results of investigations into the degradation mechanism of thermal barrier coating (TBC) applied in spark ignited and naturally aspirated diesel engines are presented. The TBC comprised 0.09 mm thick NiCrAlY bond coat and 0.36 mm thick Al_2O_3-40%TiO_2 top coat. The coating was atmospheric plasma sprayed on piston heads, inlet and outlet valves and engine head. Top coating was heavily damaged in thermal fatigue tests and in exploitation test on spark ignited engine. The mechanism of damage was spalling of the outermost layer of ceramics. Porosity of the ceramic coating increased significantly which made the coating permeable to the products of combustion and thus facilitated corrosion attack on bond layer. Spalling of coating did not increase wear of piston rings and sleeves. X-ray diffraction studies proved high phase stability of Al_2O_3-40%TiO_2 top coat. Al_2O_3-40%TiO_2 APS sprayed coating cannot be considered the alternative top coat to currently used ZrO_2-8%Y_2O_3 in engine applications

Thermal barrier coating based on Al_2O_3-40%TiO_2 can not be used for adiabatization of diesel or spark ignited engines. Al_2O_3-40%TiO_2 based TBC can be used in less demanding applications.

Keywords: *thermal barrier coating, spark ignited engine, diesel engine, phase stability, degradation mechanism*

1. Introduction

The increasing demands for higher efficiency and reduced fuel consumption have led to higher process temperatures in engines and turbines [2]. Under such working conditions, the elements which are in contact with hot gases must be either made of ceramics or protected by a ceramic layer. Ceramic materials demonstrate at high temperatures better properties than metal alloys, especially higher resistance to creep, oxidation, corrosion, lower coefficient of heat conductivity and higher resistance to abrasive and erosive wear. Trials to apply ceramic inserts to pistons of internal combustion engines failed. Since the early 70-ties, thermal barrier coatings (TBC) have been applied to gas marine and aircraft turbine combustion cans.

Plasma spraying became, because of its versality and relatively low cost, commonly applied technology to produce coatings. Plasma spraying is used to protect cylinder bores from wear. Thermally sprayed coatings have a lamellar microstructure composed of individual grains. The degree of flattening of the splat formed on impact depends on the velocity of droplets. In the spraying process, the powder of feedstock material is fed into the flame and molten droplets are accelerated to a considerable velocity. The major parameters controlling coating formation are: temperature of particles striking the substrate surface, their velocity and size distribution. Complexity of phenomena occurring in a flame spraying produces wide distribution of particle temperature and velocity. This, in turn, causes a variation of behaviour of individual droplets during impact. When spherical molten droplet impacts on the substrate it flattens adopting a shape of the disc. The portion of unsolidified material flows rapidly outwards of the impact zone and disintegrates at the disc edges into small droplets. The cooling rate during droplet solidification attains to 10^6 Ks^{-1}. Properties of the coating are thus affected by the quenching stresses. Rapidly cooled splats possess unique microstructure with such features as extension of solid state solubility, presence of metastable phases and high density of point defects. Porosity levels are in the range of a few percent through 20%, depending on the spraying method and deposition parameters. Pore size distribution found in the plasma sprayed coatings are bimodal and contain large pores of 3-10 μm size and fine pores with the size below 0.1 μm [10]. Coarse porosity is presumably associated with incomplete filling of interstices between already deposited particles. The presence of fine pores in the coating is considered the inherent feature of sprayed coatings. Pore size distribution depends on the spraying parameters and the fabrication route of the feedstock material. Porosity affects corrosion resistance, cohesion, electric resistivity and pemittivity of coatings. Another microstructural feature of coatings are cracks which run vertically to the surface (segmentation cracks) or vertically. The microstructure of plasma and detonation gun sprayed coatings was described in a number of papers [3, 9, 10]. Habib et al. [5] found that minimum porosity in the coating flame sprayed with powders from the Al_2O_3-TiO_2 system corresponds to the composition of Al_2O_3-40%TiO_2, then the major phase in the coating is Al_2TiO_5. The Al_2O_3-TiO_2 system is considered for application where large wear resistance is required.

During high temperature service, the coating system undergoes complicated microstructural transformations. Any change in porosity fraction or size distribution affects thermal conductivity and also alters strain tolerance of the coating. Deposits formed on the coatings surface can chemically react with the coating material or to seal the pores which can have detrimental effect on coating integrity. The major mechanisms of damage to coatings are: oxidation of bond layer which causes detachment of the coating and thermal stresses caused by a mismatch thermal expansion coefficients of substrate and coating.

Application of TBC's in internal combustion engines is a relatively new idea. Early theoretical studies showed that fuel consumption in diesel engines could be decreased by as much as 30%. Although results of engine tests frequently contradict each other, it is generally agreed that TBC will increase efficiency of turbocompound engines and spark ignited engines. Reoptimization of the combustion system is necessary to gain full profit from thermal insulation. Another effect which is also invoked is transparency of zirconia to infrared light which makes questionable its application in situations where heat is transported through radiation.

The stat-of-art thermal barrier coating is composed of a bond layer and the top layer sprayed with partially stabilized zirconia. The bond coat composition was adopted from MCrAlY overlay coatings used to protect components from oxidation and corrosion. Ceramic layer due to its inherent porosity can not stop aggressive species contained in the working environment from penetrating the coating. The bond coat has two functions: it protects base material from corrosion and secures good adherence of ceramic top layer. In engines burning heavy fuels which contain such contaminants as sulphur, vanadium and sodium, stabilizing oxides, e.g. Y_2O_3, can be removed from zirconia which makes is susceptible to phase transformations. Aluminium titanate is the one known chemical compound in the Al_2O_3-TiO_2 system. It crystallizes in a orthorhombic microstructure and above 1820°C it undergoes transformation into the high temperature form α-Al_2TiO_5 and congruently melts at 1860°C. The characteristic feature of β- Al_2TiO_5 is high anisotropy of thermal expansion coefficients which causes a pattern of fine cracks to appear when cooling from the fabrication temperature. Due to a presence of microcracks aluminium titanate has almost negligible thermal expansion coefficient and demonstrates very high resistance to thermal shock. The major disadvantage of this ceramics is the eutectoidal decomposition, in the range of temperatures 700-1280°C, into corundum (α-Al_2O_3) and rutile (TiO_2). However, phase stability of aluminium titanate can be rised through alloying with some oxides, namely MgO, SiO_2 or ZrO_2, which makes possible application of this material at higher temperatures. Thermally sprayed aluminium titanate is almost always considered a wear resistant material and only very few papers dealt with its potent application as a top coat in TBC [4].

The intense research into new TBC systems has been carried out, the areas of activity are:

- new top coat materials- application of rare earth element oxides to stabillize zirconia, nanostructural materials, mullite, zirconates, Cr_2O_3-ZrO_2
- new spraying methods, eg. EB-DVD, which produces chemically bonded columnar structured coating, CVD method and its variants,
- coatings with graded chemical composition,
- analytical and experimental investigations of ceramic materials and coatings.

The aim of the presented investigations was to evaluate Al_2O_3-40%TiO_2 as a top coating material.

2. Experimental methods

Phase stability investigations were carried out by means of the X-ray diffractometry method with Cu-Kα radiation. Phase compositions of the as-sprayed coating and thermally fatigued one were compared. The thermal fatigue test was carried out in accordance with the procedure developed by pistons' producer [6]. The test lasted 90 hrs and comprised 1 hr cycles. Every cycle consisted of 50 min. run at 2500 rev./min. with a brake torque of 115 Nm followed by a 10 min. run at 1000 rev./min. with a brake torque of 20 Nm. Pistons heads of naturally aspirated 4C90 diesel engine were covered by means of atmospheric plasma spraying with 0.15 mm thick NiCrAl bond layer (Cr=14-18%, Al=3-6%, Si=1.5%, Mn_{max}=2.5%, C_{max}=0.25%, Fe_{max}=1%, Ni-bal.) and 0.35 mm thick Al_2O_3-40%TiO_2 layer.

Two piston heads, cylinder head and inlet and outlet valves were plasma sprayed with 0.09 mm thick NiCrAl bond coat and 0.36 mm thick Al_2O_3-40%TiO_2 top coat. The coatings were subjected to the exploitation test in road traffic in the passenger car driven by spark ignited engine. The total mileage was 5000 km. The coatings were subsequently examined by means of optical microscopy and SEM. Fig. 1 and 2 show the coatings performed on SI engine components.

Fig. 1. Piston heads of SI engine with TBC

Fig. 2. Cylinder head of SI engine with TBC

3. Results and discussion

Results of phase composition examinations are depicted in Fig. 3 and 4. In the as-sprayed coating, the predominant phase is orthorhombic β- Al_2TiO_5 (aluminium titanate), Fig. 3. Small amounts of rutile and γ- Al_2O_3 were also found. The coating was sprayed with the atmospheric plasma spraying method, in the conditions prevailing in the torch, i.e. short residence time at high temperatures followed by rapid cooling at a rate of 10^5-10^6 K/s aluminium titanate is formed. In the coating exposed to thermal fatigue test a slight increase in the background intensity was found which indicated partial amorphization of the coating, Fig. 4. The extent of phase changes testifies to high phase stability of the coating.

Figures 5 and 6 show the TBC on piston heads after thermal fatigue test (Fig. 5) and the exploitation test on SI engine. Both pistons are covered with thick layer of soot, no spallation of coatings was stated. However durability of thermal barrier coatings performed on cylinder head and outlet valves was much worse. Coating on the outlet valve detached completely, TBC on cylinder head became liable to spalling.

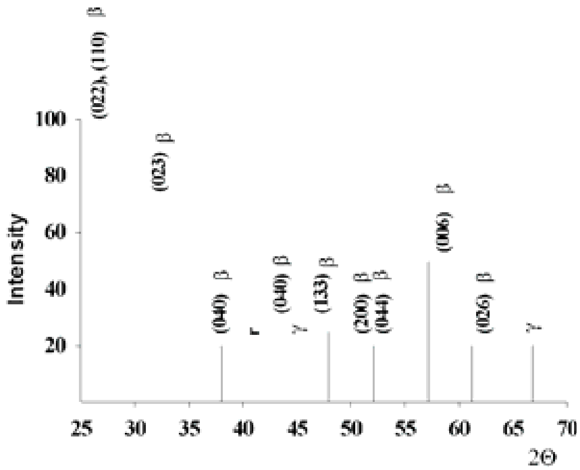

Fig. 3. Diffraction pattern of as-sprayed coating: r-rutile, γ- Al_2O_3, β- Al_2TiO_5

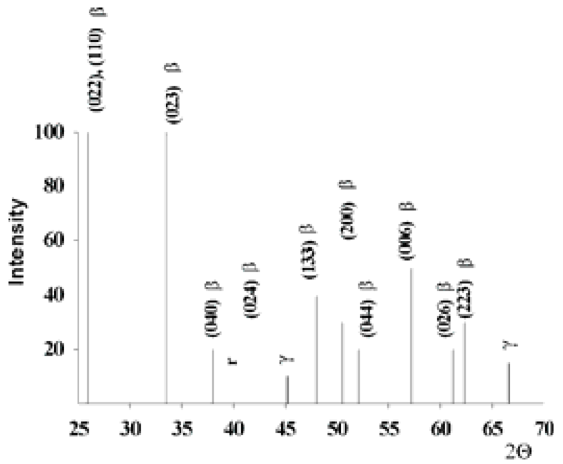

Fig. 4. Diffraction pattern of coating after TF test: r-rutile, γ- Al_2O_3, β- Al_2TiO_5

Fig. 5. Piston head of diesel engine with TBC after test

Fig. 6. Si engine piston head with TBC after thermal fatigue test

Results of SEM investigations of damage mechanisms of coatings are shown in Fig. 7-12. Fig. 7 shows the two-layered NiCrAl/Al_2O_3-40%TiO_2 coating. Top coating is of good quality with limited porosity and with no visible segmentation cracks. The AK12 substrate was blasted with

SiC prior to coating deposition which increased adherence of coating to the substrate. Fig. 8 shows the as-sprayed NiCrAl/ZrO_2-8%Y_2O_3 coating, higher volume fraction of pores than in the former case is noticed. This coating also behaved well in thermal fatigue tests. Fig. 9 shows the NiCrAl/Al_2O_3-40%TiO_2 coating after exploitation test on SI engine. The coating is covered with thick soot layer. The porosity content is much higher than in the as-sprayed coating (Fig. 7) numerous crack propagate close to the free surface. The mechanism of damage is illustrated in the next figure (Fig. 10). Chemistry of coating is altered some oxide inclusions are seen in the coating. Penetration of working environment constituents into the coating disrupted the it. Fig. 11 presents the NiCrAl/Al_2O_3-40%TiO_2 coating after thermal fatigue test. Thick soot layer on the top is seen. The mechanism of coating degradation is spalling of the outermost coating layer. Cracks propagate parallel to the surface. Higher porosity appears in the coating compared to as-sprayed condition. There is some evidence of corrosion attack on the bond layer. Fig. 12 shows the inlet valve after the test, lesser damage than in the former case is seen.

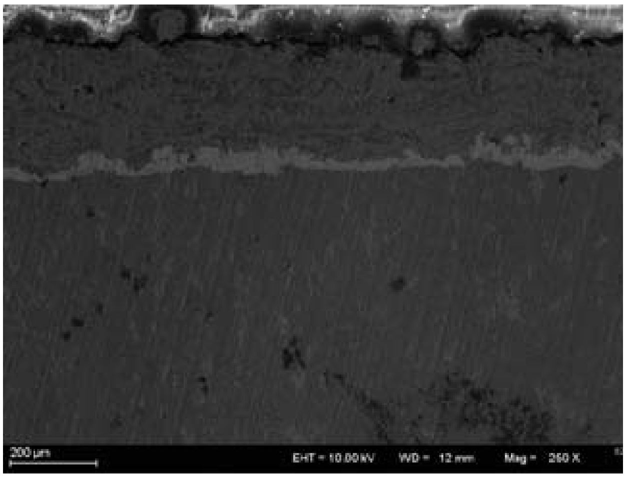

Fig. 7. As-sprayed NiCrAl/Al_2O_3-40%TiO_2 coating

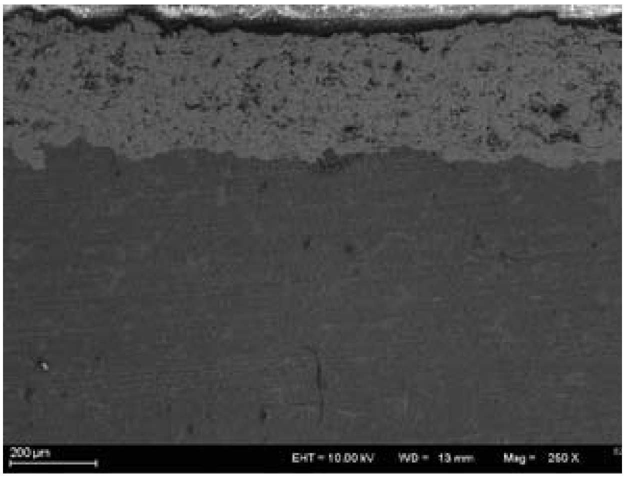

Fig. 8. As-sprayed NiCrAl/ZrO_2-8%Y_2O_3 coating

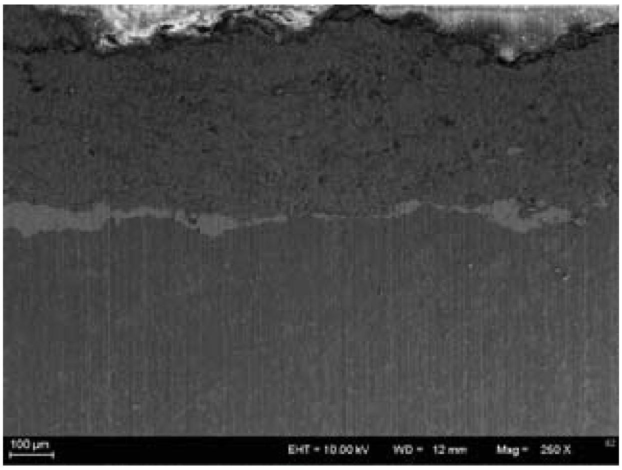

Fig. 9. NiCrAl/Al_2O_3-40%TiO_2 after exploitation test

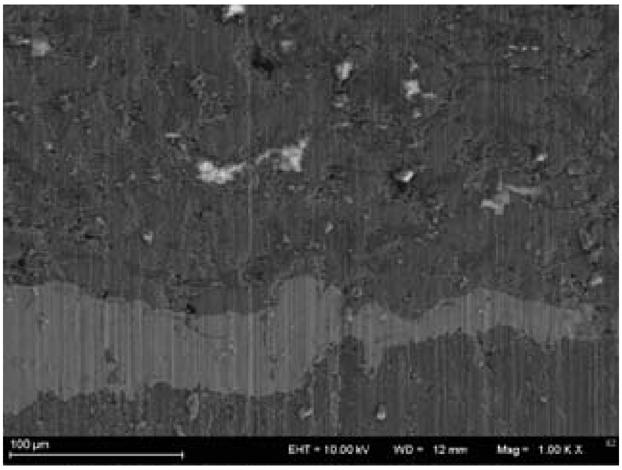

Fig. 10. NiCrAl/Al_2O_3-40%TiO_2 after exploitation test

4. Conclusio

Thermal barrier coating based on Al_2O_3-40%TiO_2 can not be used for adiabatization of diesel or spark ignited engines. Al_2O_3-40%TiO_2 based TBC can be used in less demanding applications. It seems justified to explore the possibility of performing cermet coatings cotaining Al_2O_3-40%TiO_2 as reinforcing particles. The degradation mechanism of TBC was mostly spalling of ceramic top layer.

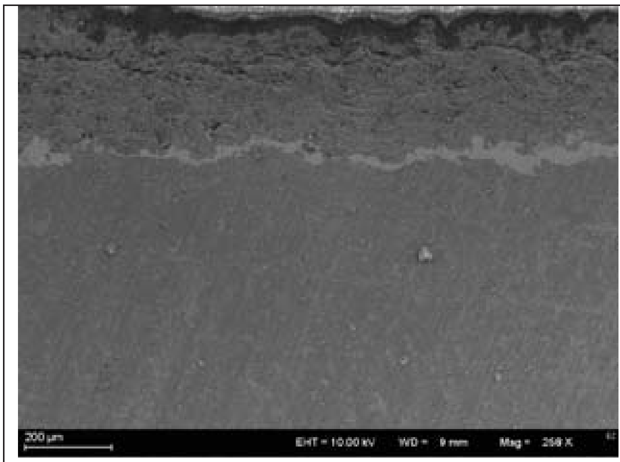

Fig. 11. NiCrAl/Al_2O_3-40%TiO_2 after thermal fatigue test

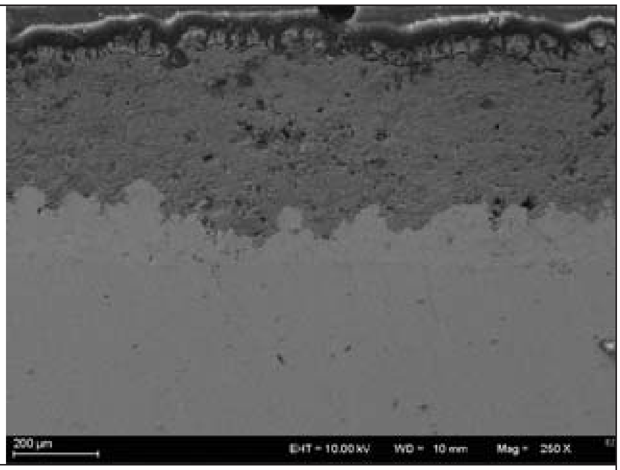

Fig. 12. SI engine inlet valve after exploitation test

References

[1] Beardsley, M. B., *Thick thermal barrier coatings for diesel engine*, Journal of Thermal Spray Technology, Vol. 6, No.2, p.181-186, 1997.

[2] Beele, W., Marijnissen, G., van Lieshout, A., *The evolution of thermal barrier coatings- status and upcoming solutions for today's key issues,* Surface and Coating Technology, Vol. 120-121, pp. 61-67, 1999.

[3] Ctibor, P., Lechnova, R., Beneš, V., *Quantitative analysis of pores of two types in a plasma-sprayed coating*, Materials Characterization, Vol. 56, pp. 297-304, 2006.

[4] Gorski, L., *Phase transformations in Al_2O_3- base ceramic materials during plasma spraying and annealing*, Materials Engineering, Vol. 16, No. 1, pp. 19-22, 1995.

[5] Habib, K. A., Saura, J. J., Ferrer, C., Damra, M. S., Gimenez, E., Cabedo, L., *Comparison of flame sprayed Al_2O_3/TiO_2 coatings: Their microstructure, mechanical properties and tribology behavior*, Surface and Coatings Technology, Vol. 201, pp. 1436-1443, 2006.

[6] Hejwowski, T., Weroński, A., *The effect of thermal barrier coatings on diesel engine performance*, Vacuum, Vol. 65, pp. 427-432, 2002.

[7] Hejwowski, T., *Treatise on wear and thermal fatigue of machine components and fabrication of structures with advantageous properties*, Lublin University of Technology Press, (in Polish) 2003.

[8] Levi C. G., *Emerging materials and processes for thermal barrier systems*, Current Opinion in Solid State and Materials Science, Vol. 8, pp. 77-91, 2004.

[9] Li, C.-J., Ohmori, A., *The lamellar structure of a detonation gun sprayed Al_2O_3 coating, Surface Coating and Technology*, Vol. 81, pp. 254-258, 1996.

[10] McPherson, R., *A review of microstructure and properties of plasma sprayed coatings*, Surface and Coatings Technology, Vol. 39/40, pp. 173-181, 1989.

[11] Soltani, R., Samadi, H., Garcia, E., Coyle, T. W., *Development of alternative thermal barrier coatings for diesel engines,* SAE Technical Paper series 2005-01-650, 2005.