Canute Sherwin[1], Kandavalli Raju[2]*

[1]Atria University, Bengaluru, India – 560 024,
[2]St Joseph Engineering College, Mangaluru, India – 575 028

Review paper
ISSN 0351-9465, E-ISSN 2466-2585
https://doi.org/10.62638/ZasMat1066

Zastita Materijala 65 ( )
(2024)

Advancements in thermal barrier coatings for internal combustion (IC) engines

ABSTRACT

Pistons of diesel engines are made of aluminum alloys. There has always been a need to increase the thermal efficiency of engines which use these pistons. Aluminum Alloy pistons find their application because they are lightweight and have a comparatively good heat transfer ability and strength to weight ratio. However, aluminum alloys exhibit increased coefficient of thermal expansion, low durability at high temperatures, increased wear rates and formation of aluminum oxide due to interaction with oxygen in air at high temperatures. These challenges are solved by coating a ceramic material onto the piston, known as the thermal barrier coatings (TBCs), due to its low specific heat and heat transfer properties. TBCs play an important role in improving the effectiveness of elevated temperatures in industrial applications like gas turbines, automobiles and aeronautical systems. TBCs tend to quickly reduce the upper surface temperature of the piston crown. This paper highlights the prominent methods of producing thermal barrier coatings including Diffusion coating, thermal spray technique, Electric Arc Wire Spray Technique, PVD, CVD, Electrodeposition and Additive Manufacturing Method. The crucial discussion is on the materials and emerging trends in developing an efficient thermal protection system. Additionally, the review throws light on employing novel materials like advanced ceramics, alloys and nanocomposites for their impact as TBCs. The paper also focuses on future prospects and current challenges in research and development of TBCs. Factors such as thermal conductivity, environmental stability and manufacturing processes are evaluated to meet the demands of high temperature internal combustion (IC) engine application. Finally, this brief review combines the existing information on TBCs for engineers, practitioners and scientists to understand the present practices and contribute to the improvement in thermal protection technologies in IC engines.

Keywords: *Thermal Barrier Coatings (TBCs), Internal Combustion (IC), Air Plasma Sprays (APS), Vacuum Plasma Spray (VPS), Physical Vapor Deposition (PVD), High-Velocity Oxy-Fuel (HVOF), Suspension Plasma Spray (SPS), Sol-Gel, Ceramics.*

1. INTRODUCTION

IC engines fall under the category of high temperature applications and there is a standing need to improve the thermomechanical behavior and service life of pistons [1]. Thermal barrier coatings (TBCs) are protective coatings applied onto metallic surfaces, exposed to high temperatures, corrosive and harsh conditions. TBCs are usually ceramics or composite systems consisting of metallic and ceramic materials to enhance the thermal insulation and thermal expansion of components [2].

Corresponding author: Canute Sherwin
E-mail: canute.sherwin@atriauniversity.edu.in
Paper received: 15. 04. 2024.
Paper corrected: 24. 08. 2024.
Paper accepted: 05. 09. 2024.
Paper is available on the website: www.idk.org.rs/journal

The demand for electric cars globally has doubled over the past decade. However, the vehicle sales aspect of electric vehicles is still small in number pertaining to issues on charging infrastructure, customer satisfaction on cost and batteries [3]. Further, the electrification of transportation is primarily focused on passenger cars and two-wheeler segments [4]. IC engines are set to remain for heavy duty diesel vehicles beyond 2040 as well. Therefore, attempts to create an environmentally friendly and energy-efficient IC engine are set to continue [5]. Some innovations in this direction includes; innovative combustion systems, piezo fuel injection system (FIS) and additive manufacturing to create pistons [6].

Engine thermal management remains one of the prime innovation areas to improve engine efficiency. Reducing the losses involved in conversion of fuels chemical energy to useful work is the practice applied to enhance the efficiency of IC engines. Automobile diesel engines expel about 50-60% of energy as heat [7]. The heat transferred from within the combustion chamber to the walls, leads to reduction of work per cycle being transferred to the piston. This leads to incomplete oxidation [8].

To overcome this TBCs were infused to various components of IC engines in the 1980s. They are usually ceramic based coatings having poor heat conductivity, such as valves, liners, cylinder heads, and piston crowns, applied to the combustion chamber's surface [9]. The aim is to reduce the heat transfer from the fuel (working gas) to the cylinder walls during the combustion process by reducing thermal conductivity; thereby reducing heat lost to the coolant. This improves engine performance [10].

The most popular TBC material which is widely used today is Yttria Stabilized Zirconia (YSZ). It delivers best performance at high temperatures [11]. Using YSZ decreases engine volumetric efficiency, increases working temperature of gas leading to lower work output and poor emission characteristics. This is observed as the wall temperature remains high even during intake and compression strokes [12].

A lot of developments have taken place in recent years, especially low-temperature-conductivity thin ceramic coatings for compression, and spark ignition engines [13, 14]. A major breakthrough in TBC technology was development of Silica Reinforced Porous Anodized Aluminum (Si RPA) coating by Toyota, also known as Thermo-swing Wall Insulation Technology (TSWIN). This coating has the ability to change wall temperatures rapidly following the transient gas temperature. The TSWIN coating's low heat-capacity and low thermal conductivity lead to fast surface temperature changes, even in short cycle durations. The surface temperatures increase during combustion and decrease during intake and exhaust stroke with gas temperature. This reduces heat loss compared to traditional TBC coatings [15, 16].

Many drawbacks were observed by researchers for anodized TBCs [17-20]. High surface roughness of TBCs was observed to increase the heat transfer rate, THC emissions and reduce combustion. Along with surface roughness, imperfections, porosity and non uniformity in coating thickness, limited the benefits of TSWIN. The problem was countered by the application of a sealant of silica.

Plasma Electrolytic Oxidation (PEO) is an innovative surface coating method that overcomes many of these problems with benefits of high hardness, wear resistance, adhesion, corrosion resistance, ultra-low thermal conductivity, heat capacity and improved homogeneity in porosity, surface finish and coating thickness [21, 22].

2. THERMAL BARRIER COATINGS DESIGN

TBCs provide solutions to various problems related to thermal insulation of IC engines by lowering the thermal conductivity and improving the system's overall effectiveness. TBCs also reduce the degradation of the substrate material. The substrate, bond coat, thermally grown oxide (TGO) layer, and topcoat are the components of the TBC design. The schematic representation of the structure of TBCs is displayed in figure 1 [23].

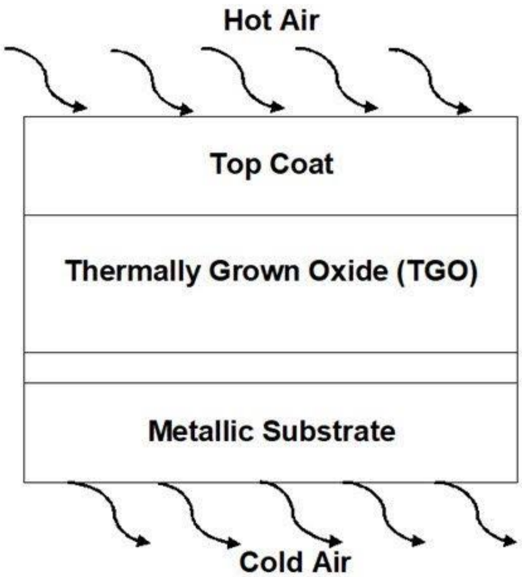

Figure 1. Schematic of TBC Design [23]

The bond coat forms an adhesive layer between the substrate and the other layers by imparting the coating's structural stability. The TGO layer is formed by diffusion of oxygen during the manufacturing stage. The top coat is a ceramic layer which protects the substrate thermally [23].

2.1. Top Coat Materials

Ideal materials for top coat should possess the following properties; phase stability, low thermal diffusivity, thermal shock resistance, strong adhesion, and corrosion resistance [24]. Some of the materials that can be considered as top coat materials include; zirconia, titania (titanium oxide), porcelain, alumina, pyrochlores, porcelanite, garnets, monazite, perovskites, lanthanum magnesium hexa-aluminate and diamond [25].

Yttria partially stabilized zirconia (YTZP) exhibiting properties like low thermal diffusivity, high dielectric constant, excellent fracture toughness and chemically inert at high temperatures is widely used [26]. Yttria-stabilized zirconia (YSZ) is observed to display higher resistance to thermal shocks compared to other ceramics viz Magnesia stabilized zirconia (MSZ), Magnesium oxide partially stabilized zirconia (Mg-PSZ), Glass-infiltrated zirconia-toughened alumina (ZTA), Zirconia-containing lithium silicate ceramics (Zls). Under applied external stress, it maintains the zirconia tetragonal phase at room temperature through a monoclinic phase transition [27]. This phase change builds up compressive stress in the vicinity of cracks, building transformational toughness. The disadvantage associated with YSZ is that its application is limited to temperatures below 1200℃ [28, 29]. This happens predominantly because of the metastable tetragonal phase transition and sinterability leading to increase in heat transfer and spallation in TBCs [30, 31].

Among the other top coat materials, Zirconates are introduced. One such alternative to YSZ is Pyrochlore $La_2Zr_2O_7$ due to low young's modulus (160–125 GPa at temperatures between 200°C and 1000°C) and thermal conductivity (1.8–3.0 W/mK at temperatures between 200°C and 1000°C) [32]. Monazite or $LaPO_4$, a topcoat material, is stable at high temperatures (around 1300°c) with high coefficient of thermal expansion and low conductivity.

The $LaTi_2Al_9O_{19}$ (LTA) system is tested for stability at high temperatures around 1300℃ and it exhibits excellent stability of phase [33]. LTA has a thermal expansion coefficient similar to YSZ. However, LTA displayed lower fracture toughness compared to YSZ. This can be solved by having a double layer of YSZ/LTA [34, 35]. Introducing dopants like Yb_2O_3, Gd_2O_3, CeO_2 etc. decreases heat conductivity and Young's modulus while preserving YSZ-like fracture toughness. The phase instability problems associated with conventional YSZ are resolved by this technique [36]. Use of few garnets like $Y_3Al_5O_{12}$ are gaining importance among researchers because of its ideal mechanical and thermal properties with phase stability and low diffusivity of oxygen [37, 38].

2.2. Bond Coat Materials

Diffusion and overlay coatings are two forms of bond coats used in TBC applications. In diffusion coatings, an intermetallic layer is diffused to form a boundary for oxygen diffusion. Aluminum coated superalloy like NiAl with silicon and chromium inclusions is one such example of diffusion bond coats [39]. Platinum-modified NiAl bond coats are presently used for many applications [40]. It is observed that for longer thermal cycles Pt-modified NiAl bond coatings work effectively, yet for smaller thermal cycles overlay coatings are proved to be better. One such prominent overlay coating is MCrAlX bond coat where X stands for Y or Zr and M for base material such as Co, Ni or Fe. M is intended to improve the substrate material's compatibility. and X helps in thermal resistivity with grown aluminum oxide and ceramic coating [41].

2.3. Thermally Grown Oxide (TGO) Layer

The TGO layer develops and grows at high temperatures between bond and ceramic top coats. Growth stresses are introduced because of differences in thermal expansion coefficients of TBC layers and continuous formation of TGO material [42].

2.4. Multi Ceramic Layer Coatings

The commonly used YSZ single layered coating exhibits short Thermal cyclic fatigue (TCF) life time. To enhance the lifetime of coatings, researchers have started working on double layered and triple layered TBCs. Using double-ceramic layer (DCL) coatings is a novel method of improving TBC performance. It is achieved by introducing Zirconate layers into YSZ top coat [43].

Zirconates like La_2Zr2O7 (LZ), $Gd_2Zr_2O_7$ (GZ) and $Nd_2Zr_2O_7$ (NZ) exhibit low thermal conductivity, high temperature for phase transformations and corrosion resistance properties but have low coefficients of thermal expansion and fracture toughness [44]. By using multiple layers of Zirconates the mismatch in thermal expansions are reduced and fracture toughness is improved [45, 46].

Mahade and Dolekar et al. [47]. compared GZ / YSZ (double layered), GZ dense / GZ / YSZ (three layered) and single-layered YSZ coatings. Single-layered YSZ coating exhibits low thermal life cycle, while the three-layered TBC exhibited the highest [47]. Also, multi layered coatings are more resistant to corrosion as tested for different molten salts [48,49]. The schematic representation is provided in figure 2.

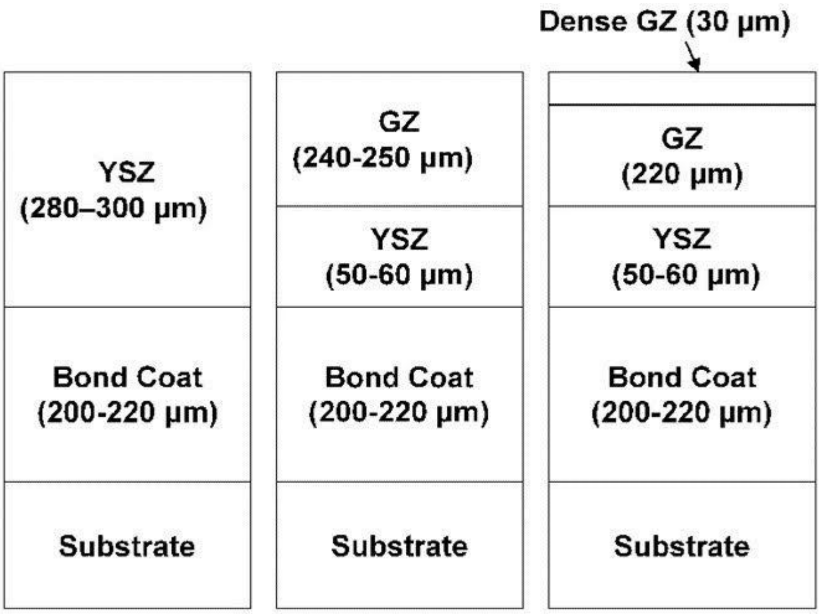

Figure 2. Coating architectures of single layered, double layered and triple layered coatings [47]

3. FABRICATION TECHNIQUES

Among the prominent TBC fabrication techniques; electric arc wire spray coating, thermal spray techniques, diffusion coating, Ni-dispersion coating, magnetron sputtering and physical vapor deposition (PVD) dominate the most. Figure 3 represents the broad classification of fabrication techniques.

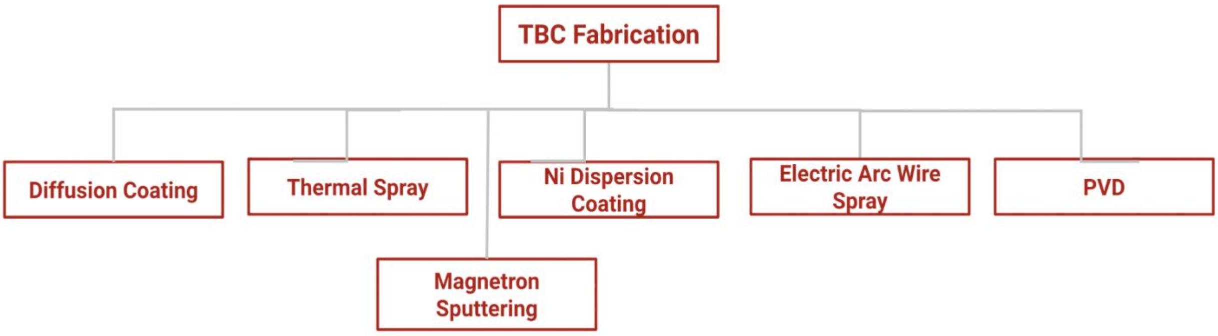

Figure 3. Broad Classification of TBC Fabrication Techniques

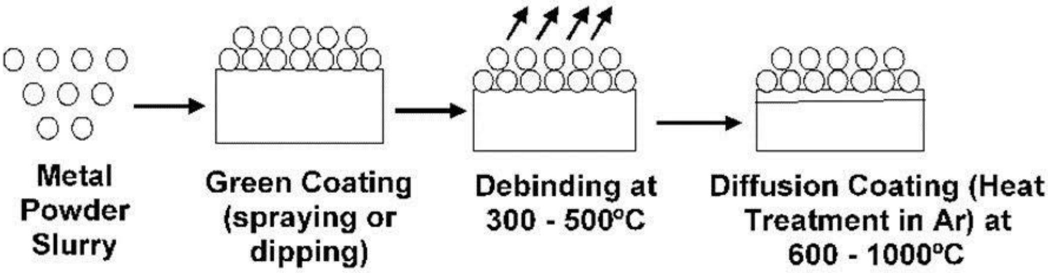

Figure 4. Diffusion Coating Process

During diffusion coating, protective materials like aluminum + silicon or aluminum + chromium are evaporated on the hot component at approximately 900°C. In this process a slurry of metal powder is initially sprayed on the base material followed by debinding and oxidation at high temperatures [50]. Figure 4 displays the diffusion coating process.

In thermal spray technique, the material of high melting point is deposited onto the substrate material using a plasma jet or HVOF method. The energy carrying media (plasma) heats and melts the feed, followed by injection in the form of rod, wire or powder. The peak velocity and pressure causes the particle droplets to flatten and deposit as layers [51]. Figure 5 displays the schematic representation of thermal spray technique.

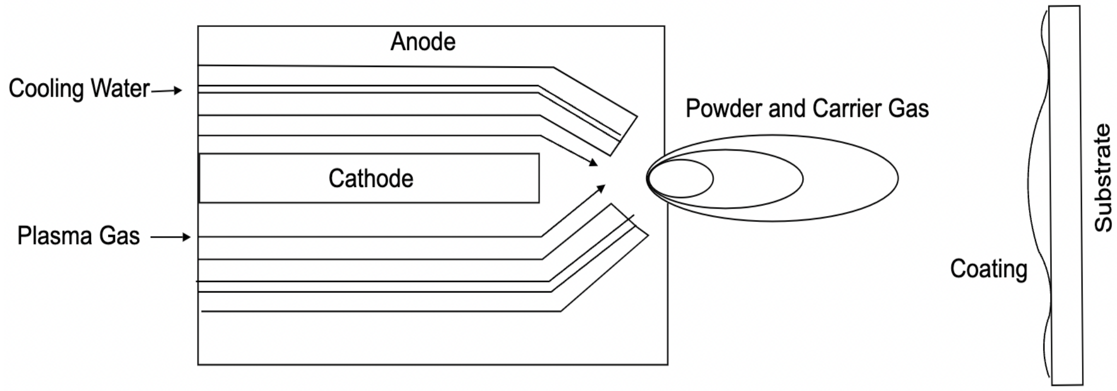

Figure 5. Schematic representation of coating process by thermal spray technique

Electric arc wire spray technique uses an electric arc which is struck between two feedstock wires. The heat generated is sufficient to melt the material. The molten metal is then transported by gas stream onto the target surface where it solidifies [52]. The schematic representation of electric arc wire spray technique is represented in figure 6.

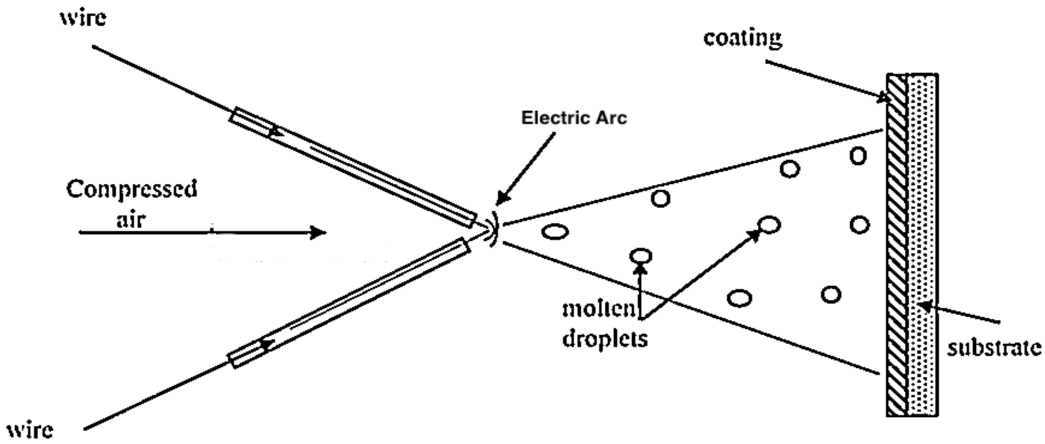

Figure 6. Schematic representation of electric arc wire spray technique

Physical Vapour Deposition (PVD) is a thermal barrier coating technique in which the material to be deposited is sublimated and evaporated into atoms or molecules and is transported towards the substrate where it is condensed. It is very much crucial to maintain the chamber under low pressure like plasma or vacuum [53]. Among the different PVD deposition techniques EB-PVD (Electron Beam-PVD) is most commonly used in industries, in which the electron beam is used to melt the target material followed by vaporizing and depositing on the surface with unique columnar microstructure [54]. Aluminium Titanium Nitride, ceramic, titanium, and zirconium are the coating materials utilized in EB-PVD [55]. The PVD process is represented in figure 7.

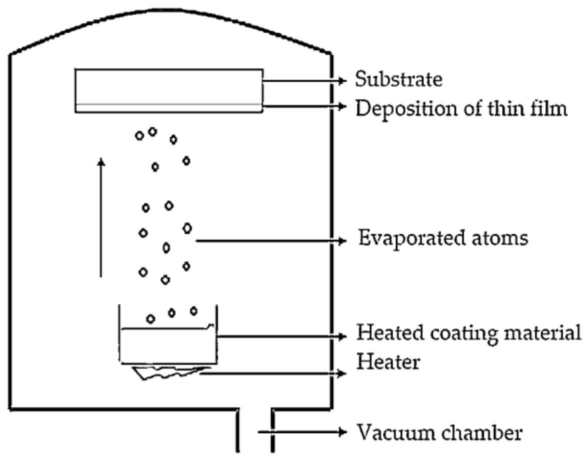

Figure 7. PVD arrangement and process

Chemical Vapour Deposition (CVD) is used to deposit thin films. The material gets deposited in vapor phase onto the heated substrate. One or more precursors are kept in a chamber throughout this process for reaction and decompose on the substrate surface as thin film [56]. Figure 8 represents a simple CVD process.

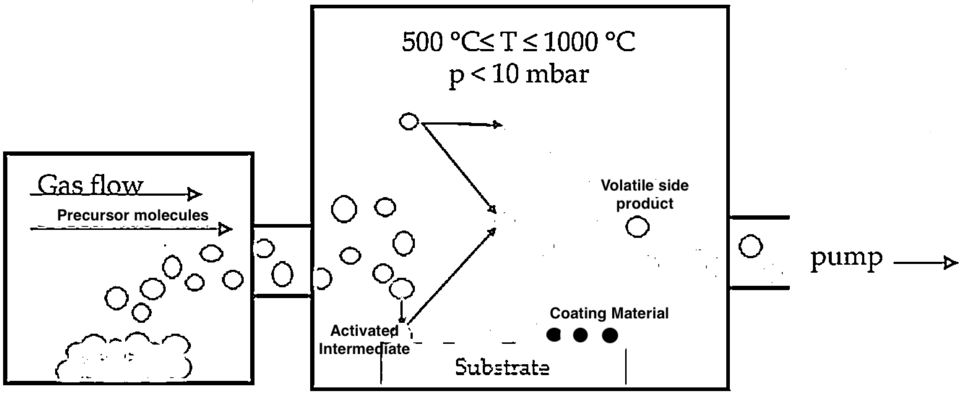

Figure 8: CVD process

Electrochemical processes are being tried recently to fabricate metal and ceramic thermal barrier coatings. The electrochemical processes are categorized as; electrophoretic and electro-deposition. In electrophoretic deposition, charged particles are deposited onto oppositely charged electrodes from a suspension source [57]. Electrolytic deposition uses soluble salt solution of the metal to be coated and deposits the oxide layer [58].

One of the latest advancements in fabricating Functionally Graded Materials (FGM) is through additive manufacturing process. Among the AM methods, material jetting, powder bed fusion, stereolithography, directed energy deposition (DED), and fused deposition modelling are presently used for thermal barrier coatings. These processes exhibit better control of process parameters [59].

4. CORROSION RESISTANCE AND MECHANICAL PROPERTIES OF THERMAL BARRIER COATINGS

Thermal barrier coatings in IC engines are aimed to operate at very high temperature and pressure. A lot of tests are being conducted to determine oxidation and mechanical properties. The properties are greatly affected because of the microstructure of coating, usually columnar and lamellar depending on coating technique. Also the parameters selected for the process like powder size, spray distance, spray rate, current etc., will have an impact [60].

Failure in TBCs occurs due to growth of TGO due to oxidation. The growth causes additional stresses leading to nucleation and propagation of microcracks between layers. Therefore, controlling the formation and thickness of TGO is critical in determining the life of TBCs. Applying ceramic layers was observed to provide higher oxidation resistance as compared to nickel based alloy material, typically used for IC engines. The coated components were tested by exposing for 100 h at 1000℃. Microstructural changes due to oxidation were observed up to the depth of 35 µm in coated samples as compared to 80 µm in as received alloy material [61].

TBCs also fail due to mismatch in thermal expansion coefficients between metals / alloys and ceramics on cooling. Crack formation can be avoided by selecting materials with almost similar thermal expansion coefficients [62]. The coatings after deposition are usually marked by a significant quantity of smooth craters. Exposure to high temperature forms needle-like features and with the exposure to corrosive environments leads to the growth of certain crystals [63].

The microstructures of coatings produced by SPS, EB-PVD methods are made of columns in the top coat (third layer of coating). The columns are thinner in comparison to other coatings. This is due to lower surface roughness and diffusion layers. This provides higher adhesion of layer particles during deposition creating more peaks. However, there is an issue of spallation due to poor bonding between SPS top coat and bond coat surface [64-66]. HVAF and diffusion coats form a dense, thin and uniform TGO layer after certain exposures to high temperatures [63]. A gradually grown TGO layer is ideal to prevent oxidation. Comparing HVAF and VPS, HVAF bond coats exhibit a 20% higher lifetime for corrosion. Comparing APS, SPS and PS-PVD TC in porous, standard and dense configurations, dense PS-PVD coating is more durable for thermal cycle fatigue and corrosion lifecycles. High column density due to much narrower column width, small intercolumnar gaps for enhanced strain tolerance, and medium intra-columnar porosity for reduced thermal conductivity are characteristics of the ideal columnar microstructure [67].

The fracture toughness is the critical factor which determines the durability of TBCs [68]. The fracture in brittle materials is initiated by thermo mechanical loading or processing defects like pores, cavities, and cracks [69]. Besides thermomechanical loading or manufacturing defects, the complex mechanical loading also leads to accelerated total failure [70].

The durability of coating is measured by the bending test, by which modulus of elasticity and fracture toughness is determined [71]. The results show that the TC elastic modulus gradually decreases for increasing temperatures. Three-point bending and micro cantilever bending are two prominent methods to analyze the strength of thermal barrier coatings [72]. Regardless of the length of heating, it is intended that ceramic coating enhance yield strength and ultimate tensile strength [73]. Higher the heating duration, higher the difference between yield strength and ultimate tensile strength [74].

5. CONCLUSIONS

The following conclusions may be drawn from the present study on Thermal Barrier coatings (TBC) for Internal Combustion (IC) engines:

- TBCs provide better solutions to various problems on thermal insulation of IC engines for improving the overall efficiency.
- The TBC design consists of a topcoat, a bond coat and a thermally grown oxide (TGO) layer
- Use of two and / or three layer coatings is a novel method of improving TBC performance.
- Besides traditional methods, Electrochemical Processes and Additive Manufacturing techniques are being explored to develop thermal barrier coatings.
- Corrosion resistance and Mechanical properties are the crucial parameters in estimating the life of thermal barrier coating.
- The finer the coating's microstructure is, the better are the corrosion resistance and mechanical properties

6. REFERENCES

[1] É. Lima, K. Costa, A. Medeiros, J. Medeiros (2006) Life Cycle Analysis of an Internal Combustion Engine Through Thermal History of the Cylinder Head and Scanning Electron Microscopy. SAE Technical Paper 2006-01-2802 https://doi.org/10.4271/2006-01-2802.

[2] N. P. Padture (2022) Thermal barrier coatings for gas-turbine engine applications. Science, 296, 280–284, https://doi.org/10.1126/science.1068609.

[3] REUTERS. Electric dream: Britain to ban new petrol and hybrid cars from 2035. Available on: https://uk.reuters.com/article/us-climate-change-accord-idUKKBN1ZX2RY. (accessed 15 Nov 2023).

[4] International Energy Agency (IEA). Global EV outlook 2019 - Scaling-up the transition to electric mobility. May 2019.

[5] International Energy Agency (IEA). The Future of trucks – Implications for energy and the environment. 2017.

[6] A. Hegab, A. La Rocca, P. Shayler (2017) Towards keeping diesel fuel supply and demand in balance: Dual-fuelling of diesel engines with natural gas. Renewable Sustainable Energy Revs, 70, 666–697, https://doi.org/10.1016/j.rser.2016.11.249.

[7] J. B. Heywood (2018) Internal combustion engine fundamentals. McGraw-Hill, New York, USA, 2nd Edition, ISBN: 9781260116106.

[8] G. Borman, K. Nishiwaki (1987) Internal-combustion engine heat transfer. Prog Energy Combust Sci, 13 (1), 1–46. https://doi.org/10.1016/0360-1285(87)90005-0.

[9] R. Kamo (1987) The adiabatic engine for advanced automotive applications, in: R. L. Evans (Ed.). Automotive Engine Alternatives, Plenum Press, New York, USA, 143–165, https://doi.org/10.1007/978-1-4757-9348-2_6.

[10] G. Woschni, W. Spindler, K. Kolesa (1987) Heat Insulation of Combustion Chamber Walls– A Measure to Decrease the Fuel Consumption of I.C, Engines?. SAE Tech Pap, 8703397, https://doi.org/10.4271/870339.

[11] S. Dhomne, A. M. Mahalle (2019) Thermal barrier coating materials for SI engine. Mater Res Technol, 8 (1), 1532–1537, https://doi.org/10.1016/j.jmrt.2018.08.002.

[12] M. Andrie, S. Kokjohn, S. Paliwal, L. S. Kamo, A. Kamo, D. Procknow (2019) Low heat capacitance thermal barrier coatings for internal combustion engines. SAE Tech Pap, 2019–01-0228, https://doi.org/10.4271/2019-01-0228.

[13] A. Kikusato, K. Terahata, K. Jin, Y. Daisho (2014) A numerical simulation study on improving the thermal efficiency of a spark ignited engine –- Part 2: predicting instantaneous combustion chamber wall temperatures, heat losses and knock. SAE Tech Pap, 2014–01-1066, https://doi.org/10.4271/2014-01-1066

[14] S. Caputo, F. Millo, G. Cifali, F. C. Pesce (2017) Numerical investigation on the effects of different thermal insulation strategies for a passenger car diesel engine. SAE Tech Pap, 2017–24-0021, https://doi.org/10.4271/2017-24-0021.

[15] H. Kosaka, Y. Wakisaka, Y. Nomura, Y. Hotta, M. Koike K. Nakakita (2013) Concept of "temperature swing heat insulation" in combustion chamber walls, and appropriate thermo-physical properties for heat insulation coat. SAE Tech Pap, 2013–01-0274, https://doi.org/10.4271/2013-01-0274.

[16] K. Fukui, Y. Wakisaka, K. Nishikawa, Y. Hattori, H. Kosaka, A. Kawaguchi (2016) Development of instantaneous temperature measurement technique for combustion chamber surface and verification of temperature swing concept. SAE Tech Pap 2016–01-0675, https://doi.org/10.4271/2016-01-0675.

[17] J. Somhorst, M. Oevermann, M. Bovo, I. Denbratt (2019) Evaluation of thermal barrier coatings and surface roughness in a single-cylinder light-duty diesel engine. Int J Engine Res, 22 (3), 1–21, https://doi.org/10.1177/1468087419875837.

[18] A. Kawaguchi, Y. Wakisaka, N. Nishikawa (2019) Thermo-swing insulation to reduce heat loss from the combustion chamber wall of a diesel engine. Int J Engine Res, 20 (7), 805–816, https://doi.org/10.1177/1468087419852013.

[19] S. Memme, J. S. Wallace (2012) The influence of thermal barrier coating surface roughness on spark-ignition engine performance and emissions. Proceedings of the ASME 2012 internal combustion engine division fall technical conference, Vancouver, BC, Canada, 23–26 September 2012, 893–905. New York: ASME. https://doi.org/10.1115/ICEF2012-92002.

[20] H. Osada, H. Watanabe, Y. Onozawa, K. Enya, N. Uchida (2017). Experimental analysis of heat-loss with different piston wall surface conditions in a heavy-duty diesel engine. Proceedings of the Comodia 9th international conference, Okayama, Japan, 25–28 July 2017. Tokyo, Japan: JSME.

[21] G. B. Darband, M. Aliofkhazraei, P. Hamghalam, N. Valizade (2017) Plasma electrolytic oxidation of magnesium and its alloys: Mechanism, properties and applications. Magnesium Alloys, 5 (1), 74–132, https://doi.org/10.1016/j.jma.2017.02.004.

[22] F. C. Walsh, C. T. J. Low, R. J. K. Wood, K. T. Stevens, J. Archer, A. R. Poeton, et al., (2013) Plasma electrolytic oxidation (PEO) for production of anodised coatings on lightweight metal (Al, Mg, Ti) alloys. Trans IMF, 87(3), 122–135, https://doi.org/10.1179/174591908X372482.

[23] M. Kunal, N. Luis, M. Downey Calvin, J. Van Rooyen Isabella (2021) Thermal barrier coatings overview: Design, manufacturing, and applications in high-temperature industries. Industrial and Engineering Chemistry Research, 60 (17), 6061-6077. https://doi.org/10.1021/acs.iecr.1c00788.

[24] E. J. Young, E. Mateeva, J. J. Moore, B. Mishra, M. Loch (2000) Low Pressure Plasma Spray Coatings. Thin Solid Films, 377−378, 788−792. https://doi.org/10.1016/S0040-6090(00)01452-8.

[25] A. K. Saini, D. Das, M. K. Pathak (2012) Thermal Barrier Coatings - Applications, Stability and Longevity Aspects. Procedia Eng. 38, 3173−3179. https://doi.org/10.1016/j.proeng.2012.06.368.

[26] X. Song, M. Xie. F. Zhou, G. Jia, X. Hao, S. An (2011) High- Temperature Thermal Properties of Yttria Fully Stabilized Zirconia Ceramics. Rare Earths, 29 (2), 155−159. https://doi.org/10.1016/S1002-0721(10)60422-X.

[27] X. Ren, W. Pan (2014), Mechanical Properties of High-Temperature- Degraded Yttria-Stabilized Zirconia. Acta Mater, 69, 397−406. https://doi.org/10.1016/j.actamat.2014.01.017.

[28] M. F. Smith, A. C. Hall, J. D. Fleetwood, P. Meyer (2011) Very Low Pressure Plasma Spray- A Review of an Emerging Technology in the Thermal Spray Community. Coatings, 1 (2), 117−132. https://doi.org/10.3390/coatings1020117.

[29] R. Hashaikeh, J. A. Szpunar (2009) Electrolytic Processing of MgO Coatings. Phys. Conf. Ser., 165, 012008. https://doi.org/10.1088/1742-6596/165/1/012008.

[30] I. Zhitomirsky (2002) Cathodic Electrodeposition of Ceramic and Organoceramic Materials Fundamental Aspects. Adv. Colloid Interface Sci., 97 (1−3), 279−317,https://doi.org/10.1016/S0001-8686(01)00068-9

[31] A. R. Boccaccini, I. Zhitomirsky (2002) Application of Electrophoretic and Electrolytic Deposition Techniques in Ceramics Processing Curr. Opin. Solid State Mater. Sci., 6 (3), 251−260. https://doi.org/10.1016/S1359-0286(02)00080-3.

[32] J. Zhang, X. Guo, Y. G. Jung, L. Li, J. Knapp (2017) Lanthanum Zirconate Based Thermal Barrier Coatings: A Review. Surf. Coat. Technol., 323, 18−29. https://doi.org/10.1016/j.surfcoat.2016.10.019.

[33] O. Sudre, J. Cheung, D. Marshall, P. Morgan, C. G. Levi (2001) Thermal Insulation Coatings of LaPO4. Ceramic Engineering and Science Proceedings; Singh, M., Jessen, T., Eds.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 22, 367−374. https://doi.org/10.1002/9780470294703.ch44.

[34] X. Xie, H. Guo, S. Gong, H. Xu (2011) Thermal Cycling Behavior and Failure Mechanism of LaTi2Al9O19/YSZ Thermal Barrier Coatings Exposed to Gas Flame. Surf. Coat. Technol., 205 (17−18), 4291−4298. https://doi.org/10.1016/j.surfcoat.2011.03.047.

[35] S. Ghosh (2015), Thermal Barrier Ceramic Coatings A Review. Advanced Ceramic Processing; Mohamed, A. M. A., Ed.; InTech, https://doi.org/10.5772/61346.

[36] W. Ma, D. Mack, J. Malzbender, R. Vaßen, D. Stöver (2008) Yb2O3 and Gd2O3 Doped Strontium Zirconate for Thermal Barrier Coatings. Eur. Ceram. Soc. 28 (16), 3071−3081. https://doi.org/10.1016/j.jeurceramsoc.2008.05.013.

[37] K. Jiang, S. Liu, X. Wang (2018) Low-Thermal-Conductivity and High-Toughness CeO2-Gd2O3 Co-Stabilized Zirconia Ceramic for Potential Thermal Barrier Coating Applications. Eur. Ceram. Soc., 38 (11), 3986−3993. https://doi.org/10.1016/j.jeurceramsoc.2018.04.065.

[38] N. P. Padture, P. G. Klemens (1997) Low Thermal Conductivity in Garnets. Am. Ceram. Soc., 80 (4), 1018−1020. https://doi.org/10.1111/j.1151-2916.1997.tb02937.x.

[39] X. Fan, B. Zou, L. Gu, C. Wang, Y. Wang, W. Huang, L. Zhu, X. Cao (2013) Investigation of the Bond Coats for Thermal Barrier Coatings on Mg Alloy. Appl. Surf. Sci., 265, 264−273, https://doi.org/10.1016/j.apsusc.2012.10.192.

[40] G. M. Kim, N. M. Yanar, E. N. Hewitt, F. S. Pettit, G. H. Meier (2002) The Effect of the Type of Thermal Exposure on the Durability of Thermal Barrier Coatings. Scr. Mater., 46 (7), 489−495, https://doi.org/10.4028/www.scientific.net/KEM.197.145

[41] M. Bai, B. Song, L. Reddy, T. Hussain (2019) Preparation of MCrAlY-Al_2O_3 Composite Coatings with Enhanced Oxidation Resistance through a Novel Powder Manufacturing Process. Therm. Spray Technol., 28 (3), 433−443. http://dx.doi.org/10.1007/s11666-019-00830-y.

[42] P. Rahul, Zh. Sulin, K. Hsia Jimmy (2003) Bond coat surface rumpling in thermal barrier coatings. Acta

Materialia, 51 (1), 239-249. https://doi.org/10.1016/S1359-6454(02)00456-8.

[43] Z. H Xu, L. M. He, R. D. Mu, S. M. He, G. H Huang, X. Q. Cao (2010) Double-Ceramic-Layer Thermal Barrier Coatings Based on La2(Zr0.7Ce0.3)2O7/La2Ce2O7 Deposited by Electron Beam- Physical Vapor Deposition. Appl. Surf. Sci., 256 (11), 3661−3668. https://doi.org/10.1016/j.apsusc.2010.01.004.

[44] R. Vassen, X. Cao, F. Tietz, D. Basu, D. Stöver (2000) Zirconates as New Materials for Thermal Barrier Coatings. Am. Ceram. Soc., 83 (8), 2023−2028. https://doi.org/10.1111/j.1151-2916.2000.tb01506.x

[45] X. Guo, Z. Lu, H-Y Park, L. Li, J. Knapp, Y-G Jung, J. Zhang (2019) Thermal Properties of $La_2Zr_2O_7$ Double-Layer Thermal Barrier Coatings. Adv. Appl. Ceram. 118 (3), 91−97, https://doi.org/10.1080/17436753.2018.1542997.

[46] E. Jordan, M. Gell (2015) Low Thermal Conductivity, High Durability Thermal Barrier Coatings for IGCC Environments. Technical Report: 1182555. https://doi.org/10.2172/1182555.

[47] S. Mahade, N. Curry, S. Bjo¨rklund, N. Markocsan, P. Nyle´n (2015) Thermal conductivity and thermal cyclic fatigue of multilayered $Gd_2Zr_2O_7$/YSZ thermal barrier coatings processed by suspension plasma spray. Surf Coat Technol., 283, 329-336, https://doi.org/10.1016/j.surfcoat.2015.11.009.

[48] S. Mahade, N. Curry, S. Bjo¨rklund, N, Markocsan, P. Nyle´n, R. Vaßen (2017) Functional performance of $Gd_2Zr_2O_7$/YSZ multi-layered thermal barrier coatings deposited by suspension plasma spray. Surf Coat Technol., 318, 208-216, https://doi.org/10.1016/j.surfcoat.2016.12.062.

[49] K. M. Doleker, H. Ahlatci, A. C. Karaoglanli (2017) Investigation of isothermal oxidation behavior of thermal barrier coatings (TBCs) consisting of YSZ and multilayered YSZ/$Gd_2Zr_2O_7$ ceramic layers. Oxid Met. 88(1–2) 109-119, https://doi.org/10.1007/s11085-016-9690-4.

[50] J. Th. Bauer, X. Montero, M. Ch. Galetz (2020) Fast heat treatment methods for al slurry diffusion coatings on alloy 800 prepared in air. Surface and Coatings Technology, 381, 125140, https://doi.org/10.1016/j.surfcoat.2019.125140.

[51] A. J. Ruys, B. A. Sutton (2021) Metal-ceramic functionally graded materials (FGMs). Metal-Reinforced Ceramics; Ruys, A.J., Ed.; Woodhead Publishing: Cambridge, UK, 327–359, https://doi.org/10.1016/B978-0-08-102869-8.00009-4

[52] E. Bakan, D. E. Mack, G. Mauer, R. Vaßen, J. Lamon, N. P. Padture (2020) High-temperature materials for power generation in gas turbines. Advanced Ceramics for Energy Conversion and Storage; Guillon, O., Ed.; Elsevier: Amsterdam, The Netherlands, 3–62, https://doi.org/10.1016/B978-0-08-102726-4.00001-6

[53] S. Mbam, S. E. Nwonu, O. A. Orelaja, U. S. Nwigwe, X. F. Gou (2019) Thin-film coating; historical evolution, conventional deposition technologies, stress-state micro/nano-level measurement/models and prospects projection: A critical review. Mater. Res. Express, 6, 122001. https:/doi.org/10.1088/2053-1591/ab5647.

[54] S-Y Qiu, C-W Wu, C-G Huang, Y. Ma, H-B Guo (2021) Microstructure Dependence of Effective Thermal Conductivity of EB-PVD TBCs. Materials, 14 (8), 1838. https://doi.org/10.3390/ma14081838.

[55] V. Miguel-Pérez, A. Martínez-Amesti, M. L. Nó, J. Calvo- Angós, M. I. Arriortua (2014) EB-PVD Deposition of Spinel Coatings on Metallic Materials and Silicon Wafers. Int. J. Hydrogen Energy, 39 (28), 15735−15745. https://doi.org/10.1016/j.ijhydene.2014.07.115.

[56] G. L. Doll, B. A. Mensah, H. Mohseni, T. W. Scharf (2009) Chemical Vapor Deposition and Atomic Layer Deposition of Coatings for Mechanical Applications. Therm. Spray Technol., 19, 510–516. https://doi.org/10.1007/s11666-009-9335-8.

[57] V. B. Mišković-Stanković (2014) Electrophoretic Deposition of Ceramic Coatings on Metal Surfaces. Electrodeposition and Surface Finishing : Fundamentals and Applications ; Djokić, S. S., Ed.; Springer New York: New York, 133−216. https://doi.org/10.1007/978-1-4939-0289-7_3.

[58] E. I. Meletis, X. Nie, F. L. Wang, J. C. Jiang (2002) Electrolytic Plasma Processing for Cleaning and Metal-Coating of Steel Surfaces. Surf. Coat. Technol., 150 (2), 246−256. https://doi.org/10.1016/S0257-8972(01)01521-3.

[59] B. E. Carroll, R. A. Otis, J. P. Borgonia, J. Suh, R. P. Dillon, A. A. Shapiro, D. C. Hofmann, Z-K Liu, A. M. Beese (2016) Functionally Graded Material of 304L Stainless Steel and Inconel 625 Fabricated by Directed Energy Deposition: Characterization and Thermodynamic Modeling. Acta Mater., 108, 46−54. https://doi.org/10.1016/j.actamat.2016.02.019.

[60] D. Kukla, M. Kopec, K. Wang, C. Senderowski, Z. L. Kowalewski (2021) Nondestructive Methodology for Identification of Local Discontinuities in Aluminide Layer-Coated MAR 247 during Its Fatigue Performance. Materials, 14, 3824. https://doi.org/10.3390/ma14143824.

[61] J. He (2022) Advanced MCrAlY alloys with doubled TBC lifetime. Surf. Coat. Technol., 448, 128931. https://doi.org/10.1016/j.surfcoat.2022.128931.

[62] T. A. Taylor, P. N. Walsh (2004) Thermal expansion of MCrAlY alloys. Surf. Coat. Technol., 177–178, 24–31.https://doi.org/10.1016/j.surfcoat.2003.05.001.

[63] M. Gupta, N. Markocsan, X. H. Li, L. Östergren (2018) Influence of Bond Coat Spray Process on Lifetime of Suspension Plasma-Sprayed Thermal Barrier Coatings. Therm. Spray Technol., 27, 84–97, https://doi.org/10.1007/s11666-017-0672-0.

N. Curry, Z. Tang, N. Markocsan, P. Nylén (2015) Influence of Bond Coat Surface Roughness on the Structure of Axial Suspension Plasma Spray Thermal Barrier Coatings—Thermal and Lifetime Performance. Surf. Coat. Technol., 268, 15–23. https://doi.org/10.1016/j.surfcoat.2014.08.067.

[64] B. Bernard, A. Quet, L. Bianchi, V. Schick, A. Joulia, A. Malié, B. Rémy (2017) Effect of Suspension Plasma-Sprayed YSZ Columnar Microstructure and Bond Coat Surface Preparation on Thermal Barrier Coating Properties. Therm. Spray Technol., 26, 1025–1037.https://doi.org/10.1007/s11666-017-0584-z.

[65] P. Sokołowski, L. Pawłowski, D. Dietrich, T. Lampke, D. Jech (2016) Advanced Microscopic Study of Suspension Plasma-Sprayed Zirconia

Coatings with Different Microstructures. Therm. Spray Technol., 25, 94–104. https://doi.org/10.1007/s11666-015-0310-7.

[66] D. Seo, K. Ogawa, T. Shoji, S. Murata (2007) Effect of Particle Size Distribution on Isothermal Oxidation Characteristics of Plasma Sprayed CoNi- and CoCrAlY Coatings. Therm. Spray Technol., 16, 954–966, https://doi.org/10.1007/s11666-007-9125-x.

[67] N. P. Padture, M. Gell, E. H. Jorda (2002) Thermal Barrier Coatings for Gas-Turbine Engine Application. Science 296, 280–284, https://doi.org/10.1126/science.1068609.

[68] M. Parchovianský, I. Parchovianská, O. Hanzel, Z. Netriová, A. Pakseresht (2022) Phase Evaluation, Mechanical Properties and Thermal Behavior of Hot-Pressed LC-YSZ Composites for TBC Applications. Materials, 15, 2839. https://doi.org/10.3390/ma15082839.

[69] A. K. Ray, E. S. Dwarakadasa, D. K. Das, V. R. Ranganath, B. Goswami, J. K. Sahu, J. D. Whittenberger (2007) Fatigue behavior of a thermal barrier coated superalloy at 800℃. Mater. Sci. Eng., A 448, 294–298. https://doi.org/10.1016/j.msea.2006.10.035.

[70] W. Zhu, Q. Wu, L. Yang, Y. C. Zho (2020) In situ characterization of high temperature elastic modulus and fracture toughness in air plasma sprayed thermal barrier coatings under bending by using digital image correlation. Ceram., Int. 46, 18526–18533, https://doi.org/10.1016/j.ceramint.2020.04.158.

[71] A. G. Evans, D. R. Mumm, J. W. Hutchinson, G. H. Meier, F. S. Pettit (2001) Mechanisms controlling the durability of thermal barrier coatings. Prog. Mater. Sci., 46, 505–553, https://doi.org/10.1016/S0079-6425(00)00020-7.

[72] Q. Wei, J. Zhu, W. Chen (2016) Anisotropic Mechanical Properties of Plasma-Sprayed Thermal Barrier Coatings at High Temperature Determined by Ultrasonic Method. Therm. Spray Technol., 25, 605–612. https://doi.org/10.1007/s11666-016-0378-8

[73] Y. Tan, A. Shyam, W. B. Choi, E. Lara-Curzio, S. Sampath (2010) Anisotropic elastic properties of thermal spray coatings determined via resonant ultrasound spectroscopy. Acta Mater., 58, 5305–5315. https://doi.org/10.1016/j.actamat.2010.06.003.

IZVOD

NAPREDOVANJE U PREMAZIMA TERMIČKE BARIJERE ZA MOTORE SA UNUTRAŠNJIM SAGOREVANJEM (IC)

Klipovi dizel motora su napravljeni od legura aluminijuma . Uvek je postojala potreba za povećanjem toplotne efikasnosti motora koji koriste ove klipove . Klipovi od aluminijumske legure nalaze svoju primenu jer su lagani i imaju relativno dobru sposobnost prenosa toplote i odnos snage i težine. Međutim, legure aluminijuma pokazuju povećan koeficijent toplotnog širenja, nisku izdržljivost na visokim temperaturama , povećanu stopu habanja i formiranje aluminijum oksida usled interakcije sa kiseonikom u vazduhu na visokim temperaturama. Ovi izazovi se rešavaju nanošenjem keramičkog materijala na klip, poznatih kao prevlake termalne barijere (TBC), zbog svojih niskih specifičnih svojstava prenosa toplote. TBC igraju važnu ulogu u poboljšanju efikasnosti povišenih temperatura u industrijskim primenama kao što su gasne turbine , automobili i vazduhoplovni sistemi. TBC imaju tendenciju da brzo smanje temperaturu gornje površine krune klipa. Ovaj rad naglašava istaknute metode proizvodnje termičkih barijernih premaza uključujući difuzioni premaz, tehniku termičkog spreja, tehniku prskanja električnim lukom, PVD, CVD, elektrodepoziciju i metodu proizvodnje aditiva. Ključna diskusija je o materijalima i trendovima koji se pojavljuju u razvoju efikasnog sistema toplotne zaštite. Pored toga, pregled baca svetlo na korišćenje novih materijala kao što su napredna keramika , legure i nanokompoziti za njihov uticaj kao TBC. Rad se, takođe, fokusira na buduće izglede i trenutne izazove u istraživanju i razvoju TBC-a. Faktori kao što su toplotna provodljivost, stabilnost životne sredine i proizvodni procesi se procenjuju kako bi se ispunili zahtevi primene motora sa unutrašnjim sagorevanjem na visokim temperaturama (IC). Konačno, ovaj kratak pregled kombinuje postojeće informacije o TBC za inženjere, praktičare i naučnike kako bi razumeli sadašnju praksu i doprineli poboljšanju tehnologija toplotne zaštite u IC motorima.

Ključne reči: *prevlake za termičku barijeru (TBC), unutrašnje sagorevanje (IC), sprejevi vazdušne plazme (APS), vakuum plazma sprej (VPS), fizičko taloženje pare (PVD), oksi-gorivo velike brzine (HVOF), suspenzija plazma sprej (SPS), Sol-Gel, Keramika.*

Pregledni rad
Rad primljen: 15.04.2024.
Rad korigovan: 24.08.2024.
Rad prihvaćen: 05.09.2024.

Canute Sherwin: https://orcid.org/0000-0002-9807-3966
Raju *Kandavalli*: https://orcid.org/0000-0002-6328-5758