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## Review Article

# Thermal barrier coating materials for SI engine

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### ABSTRACT

Ceramic coating on various parts of an internal combustion (IC) engine provides excellent thermal barrier properties which are used in preventing the heat loss during the working cycle. In case of two strokes spark-ignition engine, during the combustion in the combustion chamber (CC), due to various reasons, cent percent combustion of the charge is not possible resulting in un-burnt hydrocarbons such as CO and HC. The presence of un-burnt hydrocarbons in the exhaust gasses leads to the pollution. One of the reasons for this is heat loss in the CC. This heat loss can be saved using thermal barrier coating (TBC) on various parts of the engine. This paper discusses various TBC materials, its properties and effect on SI engines performance, combustion and emission characteristics.

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## 1. Introduction

An internal combustion engine finds its applications in various sectors like transportation, agriculture, sports, etc. This attracts a great attention by the researchers for enhancing the efficiency and performance of these engines. It has been well studied that the diesel engines are more fuel economical than that of its counterpart, SI engines. In spite of this, petrol engines have its own advantages over diesel engines on various parameters. Many researchers focused on the diesel engine with TBCs. One of the reasons for it is that they offer better fuel economy than that of SI engines. Otherwise two strokes SI have low weight and generate high power output. These engines have problem of high level exhaust emission and higher fuel consumption as compared to 4 stroke engines. This is mainly due to mixing of fresh air-fuel (charge) with exhaust gases and nearly 35% of fresh charges are lost through

exhaust valve. This is called as short circuiting phenomenon. This is the dead loss which should be avoided. Such type of short-circuiting can be avoided by adopting proper scavenging system and coating various parts of the engine like, the piston crown, CC, etc. Over and above this, the International emission regulations on engine emissions and fuel consumption have been more rigorous in recent years. These are some of the reasons why the two strokes SI engines are getting obsolete from the recent market.

Reviewing various research papers, it has been concluded that in case of internal combustion engine, most of the heat generated during combustion process is absorbed by piston and the walls of the combustion chambers. This is the direct heat loss to the piston and surrounding walls. This reduces the power generated and in turns the performance of internal combustion engine [1–3].

To overcome this problem the thermal barrier coatings are used. Using the coated piston the required temperature in the combustion chamber will be maintained. This will reduce the heat loss to the piston. This reduction in the heat loss will be used to burn the un-burnt gases thereby reducing the polluted exhaust gases [3].

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The TBC consist of a bond layer and a top coat. The bond layer is typically used to improve coating adhesion between TBC and metal substrate. Extensive research has been done on diesel engines; as the diesel engines are not susceptible to knock. Through the literature review it is evident that limited research is done on the spark-ignition (SI) engines [4].

## 2. Development of thermal barrier coatings (TBC)

Firstly, the ceramic coatings were introduced in the late 1940s and 1950s for the use in gas turbines. Turbine blade materials are nickel based alloys having melting temperatures up to 1589 K. The first application of TBCs was found to be in aerospace which was developed by National Advisory Committee for Aeronautics (NACA) and the National Bureau of Standards (NBS) [5].

In case of steam turbines also, the turbine blades are exposed to the high temperature steam which leads to oxidation, thermo-mechanical fatigue, hot corrosion and creep in the blade materials. Appropriate thickness of the coating (few hundred microns) is applied on these blades to avoid the aforesaid problems. Of course the working environment in case of steam turbines is very different than that of in IC engines. In former, the service temperature is very high, in the order of 1000–1100 °C whereas in IC engines it is less than 750 °C. The traditional turbine material reaches to its limit of temperature capabilities. Application of the TBCs will not only increases the efficiency but also reduces the requirements of the cooling system. It has been proved by various researchers that it helps in developing the overall performance of the system.

The researchers worked in this area and invented various TBCs coatings which are thoroughly discussed in this paper. While selecting any thermal barrier coating for any applications following factors have to be taken into account: (1) high melting point, (2) no phase transformation, (3) low thermal conductivity, (4) chemical inertness, (5) thermal expansion match with the metallic substrate, (6) good adherence to the metallic substrate and (7) low sintering rate of the porous microstructure [6–8].

## 3. Materials for TBCs

There exist very limited TBC materials which has the above mentioned properties. So far researchers could invent very few materials which satisfy the required properties. This paper is believed to be the first review about the ceramic TBC materials which has its application in IC engines. Here in this paper more concentration is paid by the author toward the application of the TBCs to the two stroke SI IC engines. Various TBCs which have its wider used in the targeted area are 7–8% YSZ, mullite,  $Al_2O_3$ , AlSi, NiCrAl [5,6].

### 3.1. Yttria stabilized zirconia (YSZ)

Yttria stabilized zirconia (YSZ) is one of the most popular and widely used TBC materials as it provides the best performance in high temperature zones such as diesel engines and gas

turbines. The columnar microstructure of YSZ coating provides the excellent strain tolerance and adhesion to the coating. It also has good corrosion resistant against  $Na_2SO_4$  and  $V_2O_5$ . It has been reported that YSZ can be used for the limited operation temperature (<1473 K) for long-term application, as it can generates cracks in the coating.

On the other hand, due to a high concentration of oxygen vacancies, which at high temperature assist oxygen transport and the oxidation of the bond coat at the ceramic–bond coat interface. This leads to the formation of thermally grown oxides (TGO) on the bond-coat surface. This problem has been overcome to a large extent by providing a thin oxidation-resistant layer on the bond coat such as alumina and mullite. A model of life prediction of TBCs has been developed, in which the coating failure was attributed to stresses arising from the formation of TGO [9–11].

Advantages:

- (1) High thermal expansion coefficient
- (2) Low thermal conductivity
- (3) High thermal shock resistance

Disadvantages:

- (1) Sintering above 1473 K
- (2) Phase transformation (1443 K)
- (3) Corrosion
- (4) Oxygen-transparent

### 3.2. Mullite

Mullite is an important ceramic material because of its low density, high thermal stability, stability in severe chemical environments, low thermal conductivity and favorable strength and creep behavior. It is a compound of  $SiO_2$  and  $Al_2O_3$  with composition  $3Al_2O_3 \cdot 2SiO_2$ . Compared with YSZ, mullite has a much lower thermal expansion coefficient and higher thermal conductivity, and is much more oxygen-resistant than YSZ. For the applications such as diesel engines where the surface temperatures are lower than those encountered in gas turbines and where the temperature variations across the coating are large, mullite is an excellent alternative to zirconia as a TBC material. Engine tests performed with both materials show that the life of the mullite coating in the engine is significantly longer than that of zirconia. Above 1273 K, the thermal cycling life of mullite coating is much shorter than that of YSZ. Mullite coating crystallizes at 1023–1273 K, accompanied by a volume contraction, causing cracking and de-bonding. Mullite is the most promising coating material for the SiC substrate because their thermal expansion coefficients are similar [12,13].

Advantages:

- (1) High corrosion-resistance
- (2) Low thermal conductivity
- (3) Good thermal-shock resistance below 1273 K
- (4) Not oxygen-transparent

Disadvantages:

- (1) Crystallization (1023–1273 K)
- (2) Very low thermal expansion coefficient

### 3.3. Alumina (Al<sub>2</sub>O<sub>3</sub>)

Alumina (Al<sub>2</sub>O<sub>3</sub>) is the stable phase among all aluminum oxides. It has very high hardness and chemical inertness. It has been studied that by adding certain amount of alumina in YSZ, the hardness and bond strength can be improved. On the other hand, alumina has relatively high thermal conductivity and low thermal expansion coefficient compared with YSZ. A coating of 8YSZ + Al<sub>2</sub>O<sub>3</sub> provides much longer thermal cycling life than that of YSZ alone.

Advantages:

- (1) High corrosion-resistance
- (2) High hardness
- (3) Not oxygen-transparent

Disadvantages:

- (1) phase transformation (1273 K)
- (2) high thermal conductivity
- (3) very low thermal expansion coefficient

### 3.4. AlSi

AlSi is generally used to increase the elastic modulus, enhanced heat and wear resistance properties. AlSi (15 wt%) powder used for coating on MS and SS substrates. These coating are experimented to have homogeneous distribution of SiC in AlSi matrix alloy. These also give nano size crystallites which helps in high hardness and low wear rate [14–16].

### 3.5. NiCrAl

Basically it provides the bond coat for TBCs. These materials will help in providing a strong bond between the substrate and the coating layer. The desirable coating characteristic of this material is adhesion strength, usability in the working temperature limits [17–19].

Ceramic coatings can be applied by a variety of methods, although thermal spraying techniques such as plasma spray are the most common. A bond layer with a coefficient of thermal expansion (CTE) in between that of the TBC and metal substrate is typically used to improve coating adhesion [19–22].

## 4. Alternatives

As per the study of work done by various researchers, the above mentioned TBC coating materials are used predominantly in IC engines applications. But in addition to this, there exists some other TBC materials which may prove to be advantageous in various applications. Such materials have to be explored. As explained above, TBC materials have their own

**Table 1 – Various TBC materials.**

Sr. No.	TBC material	Sr. No.	TBC material
1	ZrO <sub>2</sub>	1	Garnet (Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub> )
2	3YSZ	2	Lanthanum aluminate (LaMgAl <sub>11</sub> O <sub>19</sub> )
3	8YSZ (plasma-sprayed)	3	LaPO <sub>4</sub>
4	18YSZ	4	NiCoCrAlY (bond coat of TBC)
5	Al <sub>2</sub> O <sub>3</sub> (TGO)	5	IN737 super alloy (substrate of TBC)
6	Al <sub>2</sub> O <sub>3</sub> + TiO <sub>2</sub>	6	AlSi
7	CeO <sub>2</sub>	7	Mg-PSZ
8	La <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub>	8	Y-PSZ
9	BaZrO <sub>3</sub>	9	CaZrO <sub>3</sub>
10	TiO <sub>2</sub>	10	MgZrO <sub>3</sub>
11	Cordierite	11	Forsterite

**Table 2 – TBC materials used in IC engines.**

Sr. No.	TBC materials
1	3YSZ
2	Mullite
3	Al <sub>2</sub> O <sub>3</sub>
4	AlSi
5	NiCrAl
6	Mg-PSZ
7	Y-PSZ
8	CaZrO <sub>3</sub>
9	MgZrO <sub>3</sub>

advantages and disadvantages. To overcome this, other TBC materials are developed which are shown in Table 1 [5,6].

Amongst above, TBC materials which are suited for coating of various parts of IC engines are mentioned in Table 2.

## 5. MADM methods for TBC material selection

In the above literature it has been well studied that there exists variety of TBC material. All these materials have its own properties. Some properties are advantageous for any specific applications while the other may not. The task of selecting the best among the given lot will be very complicated if number of properties goes on increasing. On the contrary, physically applying each coating and then checking its performance is not the proper solution to the problem. In such a tricky situation, multi attribute decision making (MADM) methods will help the researcher to find the best optimal will be used. These are non traditional methods which can be used for various research problems.

Various MADM methods include weighted sum method (WSM), weighted product method (WPM), technique for order preference by similarity to ideal solution (TOPSIS), analytic hierarchy process (AHP), preference ranking organization method for enrichment evaluations (PROMETHEE), etc. among these, TOPSIS and PROMETHEE are very widely used. Both these methods give a very closest ideal preference of choices for the given data.

The TOPSIS technique gives the best optimal alternatives which have the shortest Euclidean distance from the ideal solution. It means that TOPSIS gives a solution which is not

only closest to the hypothetically best, but also farthest from the hypothetically worst.

The method, PROMETHEE, is introduced by Brans et al. [23]. The literature survey reveals that PROMETHEE has also have a lot of applications in various fields of science and technology [24]. However it had limited applications in the field of mechanical engineering. Recently in wee years its applications has been increased.

Following steps are used for the application of MADM methods.

Step 1: Preparation of Decision Table

For any given problem there may exists multiple attributes. Relevant attributes are selected such that these attributes plays a vital role as per given problem statement. These attributes namely of two types: (1) beneficial and (2) non-beneficial. For beneficial attributes, a maximum value is desirable and for non-beneficial attributes, lower values are desirable. Alternatives have the quantitative or qualitative values. The qualitative values of the attributes are needed to be converted to the quantitative using fuzzy conversions scale introduced by Chen and Hwang [25].

Step 2: Estimation of the weights or relative importance of the attributes [26].

As per the given problem statement, every attributes will have its own importance in relation to others. The quantitative correlation of these attributes with each other has to be determined. The procedure for the same is mentioned by Jee and Kang [29] and Shanian and Savadogo [30]. The procedure is further made simpler by Triantaphyllou [31] and Rao [26-28]. The weights of relative importance have to be decided by the decision maker. The decision maker must have a thorough knowledge about the problem statement and he/she should be able to justice the importance of each attribute with respect to others [27,28].

An attribute compared with itself is always assigned the value 1, so the main diagonal entries of the pair-wise comparison matrix are all 1. The numbers 3, 5, 7, and 9 correspond to the verbal judgments ‘moderate importance’, ‘strong importance’, ‘very strong importance’, and ‘absolute importance’ (with 2, 4, 6, and 8 for compromise between these values). Assuming *M* attributes, the pair-wise comparison of attribute *i* with attribute *j* yields a square matrix *B*<sub>*M*×*M*</sub> where *a<sub>ij</sub>* denotes the comparative importance of attribute *i* with respect to attribute *j*. In the matrix, *b<sub>ij</sub>* = 1 when *i*=*j* and *b<sub>ji</sub>* = 1/*b<sub>ij</sub>*.

$$B_{M \times M} = \begin{matrix} & \begin{matrix} \text{Attributes} & B_1 & B_2 & B_3 & \dots & B_M \end{matrix} \\ \begin{matrix} B_1 \\ B_2 \\ B_3 \\ \vdots \\ B_M \end{matrix} & \begin{bmatrix} 1 & b_{12} & b_{13} & \dots & b_{1M} \\ b_{21} & 1 & b_{23} & \dots & b_{2M} \\ b_{31} & b_{32} & 1 & \dots & b_{3M} \\ \vdots & \vdots & \vdots & \dots & \vdots \\ b_{M1} & b_{M2} & b_{M3} & \dots & 1 \end{bmatrix} \end{matrix}$$

Table 3 – Random index (RI) values.

Attributes	3	4	5	6	7	8	9	10
RI	0.52	0.89	1.11	1.25	1.35	1.4	1.45	1.49

Step 2.1: Authentication of the weights or relative importance of the attributes.

As decided in the above step, the weights should be correct enough to get the appropriate results. The relative normalized weight is calculated by (1) calculating the geometric mean of the *i*th row and (2) normalizing the geometric means of rows in the comparison matrix. This is represented as below:

$$GM_j = [M \prod_{j=1}^M b_{ij}]^{1/M} \text{ and}$$

$$w_j = GM_j / \sum_{j=1}^M GM_j$$

The decision maker should remember that  $\sum w_j = 1$ . because of its simplicity, easy determination of the Eigen values and reduction in inconsistency of judgments, this approach is most suitable for the decision makers.

Step 2.2: Calculate matrices A3 and A4 such that A3 = A1 \* A2 and A4 = A3/A2, where A2 = [w1, w2, ..., wj]T.

Step 2.3: Determine the maximum Eigen value λmax that is the average of matrix A4.

Step 2.4: Calculate the consistency index CI = (λmax – M)/(M – 1). The smaller the value of CI, the smaller is the deviation from the consistency.

Step 2.5: Obtain the random index (RI) for the number of attributes used in decision making as per Table 3:

Step 2.6: Calculate the consistency ratio CR = CI/RI. Usually, a CR of 0.1 or less is considered as acceptable.

Step 3: Data normalization.

Every attribute will have its own significance. These will have their own units of measure. Hence comparing them is to be avoided. Therefore these are to brought on a single benchmarking by normalizing it. Each attribute have its objective i.e. maximization or minimization. For the attribute have maximization objective, its higher value is better i.e. Profit, accuracy, etc. and for the attribute having minimization objective its lower value is preferable e.g. cost, Tool wear, etc. The desirable objectives of these attributes will vary situation to situation and problem to problem. The decision maker has to take this in account very keenly.

For beneficial attribute, the normalized values are calculated by *x<sub>ij</sub>*/*x<sub>ij</sub>*(max) where *x<sub>ij</sub>*(max) is the measure of the attribute for that has the highest measure of the attribute out of all alternatives considered. This ratio is valid for the beneficial attributes only. However for non beneficial attribute, the normalized values are calculated by *x<sub>ij</sub>*(min)/*x<sub>ij</sub>* where *x<sub>ij</sub>*(min) is the measure of the attribute for that has the lowest measure of the attribute out of all alternatives considered.

In case of TOPSIS, the normalized decision matrix is calculated as

$$R_{ij} = \frac{x_{ij}}{[\sum_{j=1}^M x_{ij}^2]^{1/2}}$$

And then calculate the weighted normalized matrix  $V_{ij}$  by multiplying each element of the column of the above matrix  $R_{ij}$  with its associate weights as explain mathematically as below:

$$V_{ij} = w_j \times R_{ij}$$

#### Step 4: Computation of preference index

Every attribute has been assigned with their weights, as explain above, and each alternative is computed with respective every attribute. The overall performance score of all the alternatives is the weighted sum which is called as the preference index. In case of SAW MADM method, the preference index is simply the weighted sum of all the attributes for that respective alternative however in case of WPM MADM method it is the weighted product of all attributes for that respective alternative.

Using various nontraditional MADM optimization methods, it is understood that the TBC material,  $Al_2O_3$  is the better choice as compare to other TBC materials for SI engine. These MADM methods provides a confirm conclusion to the researchers. The second best alternative may be Mg-PSZ TBC.

Thus selected thermal barrier coatings can be applied in the SI IC engine to insulate combustion chamber surfaces. The coatings can be applied to the entire combustion chamber or to select surfaces like the piston crown or valves. In this study the TBC coating is applied on the piston crown.

Some of the additional heat energy in the cylinder can be converted into useful work, increasing power and efficiency. Reducing heat transfer also increases exhaust gas temperatures, providing greater potential for energy recovery with a turbocharger or possibly a thermoelectric generator. Additional benefits include protection of metal combustion chamber components from thermal stresses and reduced cooling requirements. A simpler cooling system would reduce the weight and cost of the engine while improving reliability [13].

In SI engines, elevated wall temperatures can promote knock, which is auto-ignition of the homogeneous air-fuel mixture in the end gas region. As such, less insulation must be used in SI engines to avoid overly high wall temperatures. The following sub-sections summarize some of the major research that has been performed on TBCs in IC engines. In some cases the insulation was provided by means other than TBCs but with the same effect of raising surface temperatures [5]. The research work carried out by following researchers is summarized in this review [18–20].

The engine with TBC piston helps in increasing the power of the engine as stated above. This is because complete combustion of the charge in the combustion chamber which leads to minimization of emission of carbon and hydrocarbon in the exhaust gases. With this work it is proved that any two stroke engine will fit in the emission norms and hence its production can be started.

Piston coating technology for performance enhancement is a promising technique and it needs further investigation [21,22].

## 6. Conclusion

In the present study the review of the thermal barrier coating materials which can be used in IC engine application is presented with their corresponding properties. Every TBC materials have their own properties. For any application proper selection of the TBC material is require to be done. Various researchers have used different TBC materials to enhance the performance of the IC engine. It has a positive effect on the power and exhaust emission of the engine.

## Conflict of interest

The authors declare no conflicts of interest.

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