Potential applications of thermal spray coating for I.C. engine tribology: A Review

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Abstract: The IC engine has been a conventional source of producing mechanical energy for various applications. The tribopair of piston ring and cylinder liner has to work in adverse tribological conditions such as high temperature, speed and load. The wear of piston ring not only reduce the performance of the tribopair but also cause the failure of the system. The insufficient lubrication at the interface increases the tribological losses drastically. The tribological losses can be minimized by coating of some material which has superior tribological performance. The thermal spray coating can be used for providing a stable coating over the tribological surfaces. The versatile operating conditions and process parameters assist the deposition of required material to a desired thickness over the various substrate materials. The process can be used for producing the stable coating over at a faster deposition rate. The environmental friendly coating material can be used as a bled with the conventional coating material for making the process sustainable.

Keywords: Thermal spray coating; Piston ring; Tribology; HVOF; APS.

1. Introduction
The internal combustion engine (IC engine) has been used to produce mechanical energy by the burning of fossil fuels. It has been used in various applications as it can be used to produce rated power at the desired location. The mechanical efficiency of the IC engine depends primarily on the tribological characteristic of the mating surfaces. The energy loss due to friction between the cylinder liner and piston ring may be up to ≈40%. The service life of IC engine has also been affected by its tribological characteristic [1-3]. The wearing of the piston ring may lead to failure of the engine. The wear of tribopair may be due to the insufficient lubrication, increased load, speed etc. The various wear mechanism of the piston ring and cylinder liner interface has been shown in Figure 1 [4]. The reliability, efficiency and working life of IC engine depend on the tribology of piston ring and cylinder liner [5]. Hence the tribopair of piston ring and cylinder liner has been very critical from the tribological losses point of view.
The tribological performance of the IC engine depends on the working conditions, environmental conditions, lubricity etc. The variation of load, speed or working temperature affect the engine tribology considerably. The atmospheric temperature affects the heat transfer rate and flow of lubricant at the interface of piston ring and cylinder liner [6,7]. The lack of lubricity may be due to the lubricant failure, lubricant contamination, working temperature below cloud; it has been responsible for the tribological losses in the IC engine [8-10].

1.1. Piston Ring
The piston has been used to transform the chemical energy of the fuel into useful kinetic energy. Piston carries the pack of the ring including the oil ring and compression ring, arranged in series. The primary role of these rings is to provide the seal of gas between the combustion chamber and crankcase. The rings closely confirming to the grooves in the piston and cylinder, blocking the way for the gasses and unburnt fuel to move out. Piston rings have a high thermal conductivity that has been used to transfer heat from the combustion chamber to the lubricant [11,12]. The schematic diagram of piston ring has been shown in Figure 2.

The piston rings move along the cylinder liner at high sliding speed and has to be stable at high contact pressure. Figure 3 shows the brief description about the piston ring. The failure of lubricant between the piston ring and cylinder liner results in metal to metal contact, consequently increased coefficient of friction and wear [13]. The material of the piston ring should have high elasticity, corrosion resistance, high thermal conductivity, wear resistance. Cast iron and steel have been the common engineering material used as piston rings [14]. The latest advancements in piston ring have been the cast iron or steel rings coated with desired material [15].
**Figure 2:** Schematic diagram for piston ring and cylinder liner interface

**Figure 3.** Brief description of piston ring

### Functions
- Sealing
- Heat Transfer
- Support and control movement of piston
- Prevent excess of lubricant moving out of combustion chamber

### Material
- Elasticity, corrosion resistance, high thermal conductivity, wear resistance
- Cast Iron, Steel.

### Sealing ability
- Conformability
- Counter surface effect
- Blow-by prevention
- Decrease oil consumption and emissions

### Type
- Oil Ring
- Compression Ring
2. Coating techniques

Coating techniques for protecting the substrate material form atmosphere have been used from ancient times. The advanced coating methods not only protect the substrate but enhancing the performance of the substrate. The advanced coating techniques enable multiple effects like protection from corrosion and erosion, reduction in wear, achieve desired friction by inducing desired hardness, atmospheric inertness, depositing desired material over the substrate and reinforcing the substrate material etc. [16-20]. There are various coating methods like PVD, CVD, Sol-gel, Electroplating and Thermal Spray each having its advantages and drawback in the field of application as shown in Table 1 [21]. Some of the coatings are easy to achieve and cost-effective but the purpose is to provide a layer of desired material for atmospheric protection or aesthetics. The material subjected to dynamic load, erosion, wear and friction has to be coated such that the coating should service the adverse working conditions [22-25].

| Process              | Merits                                                                 | Demerits                                                                 |
|----------------------|------------------------------------------------------------------------|--------------------------------------------------------------------------|
| Thermal spray deposition | (i) Low cost and high deposition rate  
                     (ii) Applicable to variety of substrate materials.  
                     (iii) Can be widely used for numerous coating material. | (i) Irregularity of Coating thickness  
                     (ii) Residual stress concentration in coated specimen is high  
                     (iii) Difficulty in Nano porous coating. |
| Electro-deposition   | (i) Moderate deposition rate  
                     (ii) Coating matrix can be controlled  
                     (iii) Minimized porosity in the coating. | (i) Caustic waste  
                     (ii) Lower strength of coating |
| Physical vapor deposition | (i) Can coat complex materials.  
                     (ii) dense coating of Nano scale thickness  
                     (iii) preferred for insulating coating as tribological performance is not good. | (i) very low deposition rate  
                     (ii) high initial cost  
                     (iii) low strength of coating |
| Chemical vapor deposition | (i) Uniform deposition on complex shape  
                     (ii) Can coat complex materials.  
                     (iii) Porosity free coating  
                     (iv) Controlled and uniform thickness | (i) Restricted to chemical composition and use of volatile gases  
                     (ii) the very low deposition rate  
                     (iii) high initial cost |

Thermal spray coating has emerged as one such coating techniques in which the coating material has been sprayed over the substrate material at high temperature (upto 15000°C), the flow of particles is assisted by high-velocity gas/air. Classification of various thermal spray coating techniques is depending on heat source i.e. plasma spray coating, high-velocity oxyfuel coating (HVOF), arc spray coating [26-29].

The most common thermal spray coating method is Plasma spray coating, in this method the temperature of the heat source is more than 15000°C. The molten accelerated particles of coating material move towards the substrate and strike the substrate with a governed speed. The continuous bombardment of the particles on the substrate resulted in the formation of a dense layer of coating [30,31]. The coating density in the case of HVOF and arc spray coating is less as compared to plasma spray coating. High heat in the case of plasma spray coating resulted in stress-induced to the specimen. The thermal spray coating can be applied to a wide variety of substrate and coating material such as metals, ceramics, polymers, composites etc. The multilayer coating of the same or different compositions can also be achieved via thermal spray coating [32,33].
3. Thermal Spray Coating

The coating materials like Fe, Ni, WS\textsubscript{2}, oxides of Al, Fe, Cr, graphite and some polymeric materials etc. have been employed successfully for tribological improvement. The researchers have also used some special textures on the tribopairs to increase the lubricant embeddability and retention. The tribological improvements like advanced lubricant or surface textures are suitable for normal working conditions. But the adverse working conditions like operating at ultra-low temperature, the lubricant would not be functional for the initial start of the vehicle which causes a very high wear and friction and ultimately responsible for the failure of the tribopair. In such conditions, the wear resistance and self-lubricating coatings are required to improve the tribological performance. Therefore, a versatile coating is required to be deposited on substrates [34]. For deposition of these type of coatings on light metal alloys, the thermal spray processes (APS, HVOF and wire arc process) is one of the few available processes [35].

High hardness results in high wear resistance and reduced friction coefficient of the coatings. Researchers have studied the tribological behavior of APS coatings on various counter bodies from conventional steel to composite-based coatings [36-40]. High wear and friction resistance have been shown by the coatings of metallic, ceramic (carbides, nitrides and oxides) and composite based materials compared to conventional materials (cast iron) of piston rings and liners [41]. Most of the tribological tests were carried out in dry conditions few of them in lubricated conditions including the study of different anti-wear additives and friction modifiers.

The conventional processes can be used for coating the substrate material but the issue with such coating processes is that either the coating layer is not stable (as in the case of vapor deposition method) or the induced thermal stresses in the material which may result in mechanical failure of the substrate material. These issues can be addressed by the hybrid coating process. The process will be designed in such a way that it could address the tribological issues at ultra-low temperature and provide strength to the substrate material to avoid premature mechanical failure.

The prime objective for the selection of any coating process is the stability, enhanced mechanical properties of the substrate, lesser defects versatile process and environment friendly. The coating should be such that it consists of required characteristics like high hardness and wear resistance, low coefficient of friction, corrosion and erosion resistance to the substrate. The thermal spray coating for tribological improvement has been studied for developing lead plates for the batteries. Since then the thermal spray coating has been used for different applications. The various thermal spray coating methods have been used for enhancing the wear and friction resistance of the substrate material [42].

HVOF thermal spray coating can be used for a variety of substrate and coating materials for producing high density coating used for the applications especially corrosion and wear resistance [43]. The coating materials like Al\textsubscript{2}O\textsubscript{3}, iron oxide, [44] 25 wt% alumina coating [45], carbides, ceramic oxides, bromides [46-48] had their unique effect mechanical, chemical and tribological performance of the substrate. Plasma spray coating having flame temperature and cooling rate higher than the HVOF coating can be used to produce denser coating [49,50]. The amorphous and crystalline structure of coating depends on the gas pressure [51]. The size of coating material affects the mechanical behaviours of coating, the nano size coating material showed improved mechanical properties [52,53].

In arc spray method the two wires are short-circuited and the atomized material is blown on to the substrate by high velocity air. The porosity of the coating is around 2% with improved tribological behaviour of the substrate material.

The thermal spray coating can be used for a variety of substrate and coating material for producing both soft and hard coating. The coating materials like MoS\textsubscript{2} and graphite can be used for obtaining anti-friction coatings with enhanced wear resistance and self-lubricating ability [54,55]. The oxide of chromium can be used to enhance the hardness and wear resistance [56]. The high temperature tribological performance can be enhanced by coating the substrate using Ni, Al, WS\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3} and DLC coating. The polymeric coating materials like PAO, PU and Nylon not only enhanced the wear resistance but reduced the coefficient of friction considerably [57-59]. HVOF thermal spray coating on the iron based substrate material with different composition of coating materials had influenced the tribological behaviour of substrate material. The plasma spray coating had been used successfully for depositing a
A stable coating of single and multi-material. The coated material was investigated for tribological and morphological analysis and the results showed improvement in wear resistance of the coated material. The thermal spray coating had also been used for the improvement of oxidation and erosion resistance of material [60-65].

Table 2. Effect of various coating processes and materials on the different properties of substrate materials

| Name of Researcher | Coating Technique | Coating material | Substrate material | Morphology | Result |
|--------------------|-------------------|------------------|--------------------|------------|--------|
| Bo Song et.al. (2020) [66] | HVOF | WC-CrxCy-Ni and WC-Co-Cr had spherical morphology | 410 Stainless Steel | WC particles were decarburized and embedded in Ni and Cr matrix. High impact of particles removed the porosity. | WC-CrxCy-Ni coating shows better wear performance than the WC-Co-Cr coating at high temperature but inferior wear performance at room temperature at lower loads. |
| N. Abu-warda et.al. (2020) [67] | HVOF | Ni20Cr | T24 steel pipes | Coating material had spherical morphology with necks. The coating free from porosity was obtained at slower gun speed and at higher gun speed the porosity was present in the coating. | 260 μm coating thickness was achieved and it eliminated the high temperature oxidation of T24, the micro-hardness of the coated sample was measured around 460 HV and adhesive strength 29 MPa. |
| J. Singh et.al. (2019) [68] | HVOF | WC-Co-Cr synergized with Mo2C/Y2O3/ZrO2 | Stainless Steel (SDSS) 2507 | The coating thickness fluctuated from 155-185 μm. The interface of coating substrate had some voids and cracks. | The coating enhanced the corrosion and erosion resistance of the substrate material. |
| Authors                  | Process | Material                  | Coating Properties                                                                 | Comments                                                                 |
|-------------------------|---------|---------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------|
| W. Wen et al. (2019) [69] | HVOF    | CoNiCrAlY Mild Steel     | Achieved coating was heterogeneous in nature with random porosity.                  | Overall mechanical properties of the coated sample were better than the substrate. |
| J. Pulsford et al. (2019) [70] | HVOAF   | WC-10Co-4Cr 416 stainless steel | The coating material had annular morphology. Very little porosity was present in the coated samples. WC appeared as brightest phase uniformly distributed throughout the surface. | Coating enhanced the microhardness of the substrate material. The dry tribological performance of the coated sample also improved. |
| I. Rodrigues (2020) [71] | HVOF    | Cr:C2-25(80Ni20Cr) 316 L SS | The coating thickness observed around 380 μm. The distribution of coating material was uniform, Ni and Cr acquired annular morphology after coating. There was porosity also present in the coating. | The tribological performance of coated material improved in both dry and in presence of water NaCl. There was increase in wear rate observed in presence of NaCl + H2SO4 solution. |
| V. Matikainen et al. (2020) [72] | HVOF and HVAF | Cr:C2-25NiCr, Cr:C2-50NiCrMoNb, Cr:C2-37WC-18NiCoCr and WC-10Co-4Cr | The coating material had a mixed morphology i.e. spherical morphology along with agglomerated and sintered. The porosity of HVAF coating was less than the HVOF coating. The HVAF coating Elastic modulus, wear, cavitation and erosion resistance of HVAF coating was higher than HVOF. High Cr and presence of WC increased enhanced the |
| Source                                    | Process | Composition  | Microstructure/Property Differences                                                                 |
|------------------------------------------|---------|--------------|-----------------------------------------------------------------------------------------------------|
| P. Robert. et al. (2019) [73]            | ASP, FS | Babbitt (ASTM B23/2) | Low Carbon Steel with higher cooling rate promoting refined microstructure. The COF of coated samples was higher in dry condition and lower in lubricated conditions compared to casted samples. The wear rate of coated samples was lower. |
| A. Sharma et al. (2020) [74]             | APS, HVOF | Cr3C2-NiCr; T-800; PS-400 Hastelloy-X and Inconel X-750 | T800 had highest wear rate where as PS400 had lowest. The presence of glaze oxide layer was responsible for that reduction. The COF in case of PS400 was lowest. |
| Z. Zhang et al. (2019) [77]              | APS, HVOF | Ni60 and 17Co 17-4PH stainless steel | The APS coated samples had layered structure, whereas the HVOF coated had more uniform structure. The voids and porosity was more in case of APS. |
| C. I. Pruncu et al. (2017) [75]          | cathodic arc technique | Zr, Nb and Si doped TiCN stainless steel and Si wafer | The coating had face centred cubic structure. The coatings had low porosity and good WDE resistance. HVOF-WC17Co coating material has the best WDE resistance, which shows 50.6% less volume loss than that of the substrate material. |
| Source                  | Coating Method | Coating Composition | Substrate | Coating Properties                                                  |
|------------------------|----------------|---------------------|------------|---------------------------------------------------------------------|
| D. D. LaGrange et al.  | Cathodic arc   | Nb–Ti–N             | AISI D2    | Excellent corrosion resistance due to low residual stresses. TiCN coating had better tribological performance at elevated temperature. |
|                        |                |                     |            |                                                                     |
| J.V. Pimentel et al.   | R.f. magnetron | W–S–C–Cr            | AISI D2    | Low COF and wear rate was observed in case of coated specimen. The surface roughness acted as seat for the wear debris. |
|                        | sputtering     |                     |            |                                                                     |
| N.W. Khun et al.       | APS            | Hydroxyapatite (HA) | Ti6Al4V    | The coating deposited at higher in-flight particle velocity had lower COF and wear rate whereas, the coating with low in-flight velocity had low COF and higher wear rate. |
| W. Deng et al.         | APS            | 8YSZ-C/MoS2 Stainless steel |            | The MoS₂ was uniformly worn and the wear mechanism was three-body wear mechanism. |

The nitride debris resulted in three body wear mechanism. The overall tribological performance of the coated samples was enhanced by modification of deposition conditions.
The microstructure of coated surface was porous and the presence of C & MoS$_2$ was seen in the pours. The presence of coated materials was detected in XRD and Raman spectroscopy. The tribological performance of C or MoS$_2$ blended coating was better compared to 8YSZ coating due to decreased porosity.

| Authors                  | Method      | Coating Material | Details |
|--------------------------|-------------|------------------|---------|
| A. Çelik et al. (2020)   | Sol-gel     | B+TiO$_2$        | Ti6Al4V | The presence of B and TiO$_2$ was observed in the XRD analysis. The contact angle increased as the TiO$_2$ was doped with B. The COF and wear rate reduced up to 72% and 68% respectively as a result of increased hardness. |
| B. Venkateshwarlu et al. (2019) | Plasma spray | Nano TiC-Co AISI 1020 steel | The inter splat bonding was weak and the unmelted particles were present. The decarburization of WC resulted in dominating W phase observed in XRD. The COF and wear increased with increase in load and speed. The low CPSP coating had better tribological performance compared to the high CPSP. |
| X. Zhao et al. (2016)    | APS         | Ni-Graphite doped 3Al$_2$O$_3$-2SiO$_2$ Austenitic stainless steel | The presence of Al$_2$O$_3$ & SiO$_2$ was seen along with the amorphous hump in XRD. The coating had high roughness and porosity. The COF and wear rate was low at lower load. At higher loads the splats tried to come out due to weak bonding resulting in poor tribological performance. |
4. Discussion and future direction
Thermal spray coating contributes a major portion of recent development in the engine tribology. The purpose of coating the tribopair introduce the desired physical and chemical properties in the material. The coated surfaces result in efficient mechanical system with enhanced life cycle. Sufficient efforts are required to be undertaken for the development of cost effective, eco-friendly coating to enhance the tribological performance of the piston ring. The researches have emphasized on only one aspect i.e. wear of the piston ring. A little effort has been made to produce a coating for reducing the coefficient of friction and wear simultaneously. More effort is needed to develop the multi-layer hybrid eco-friendly composite coating to make the process sustainable.

5. Conclusions
The failure of piston rings and cylinder liner tribo-pair could result in power loss, higher emissions, low thermal efficiency, high fuel consumption etc.; all these issues make it highly critical. The surface enrichment of the tribopair has been a successful tool for improving tribological performance. The thermal spray coating can be employed to a variety of substrate material to produce the stable coating of desired material as compared to other deposition techniques. The thermal spray coating not only enhances the tribological performance of the tribopair but also embeds the desired thermal, mechanical, chemical and electrical properties. The tribological performance of the piston ring can be enhanced by depositing a layer of desired material having thickness in microns through the cost-effective thermal spray coating. The coating process can be designed for sustainability by introducing the environment friendly materials as a blend with the conventional material.

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