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Significance and Properties of Coatings

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M.Sc. Motorcycle Engineering

Mechanisms of Material Failure

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1.Abstract

Modern metallic components are designed to utilize the optimum performance of the product in operation where the material operates under varying operating conditions as a function of environment. Operating conditions have direct contribution in damaging the surface characteristics as the material substrate is exposed to the biological and physiochemical environment where enzymes catalyse non spontaneous chemical reaction resulting in degradation of metallic components by surface reaction. This is be due to enzymatic chemical reactions on the substrate influenced by Enzyme concentration, substrate concentration, PH value due to fluidity, operating temperature, Effectors and Inhibitors initiating catalyst function increasing the rate of reaction. Coating of substrates provides resistance against the moisture penetration increasing the productivity over a long run by acting as a barrier between atmosphere and substrate. Hence it is vital for a coating to ensure high performance characteristics in an aggressive environment providing resistance to weathering, humidity, corrosion alongside superior mechanical properties as abrasion, impact strength and hardness.

This report will investigate the significance of iron carbon coating on a lightweight Aluminium silicate cylinder block liner substrate of an internal combustion engine subjected to degradation parameters such as atmospheric reactants, chemicals in automotive fuel and engine oil. The reliability of the powerplant is achieved by twin wire arc spraying method providing durability and protection with surface finish for a modern powerplant with improved wear characteristics and pollution control.

2.Introduction

2.1 Cylinder Block Liner

Regardless of the fact that air pollutants, automotive fuels, and lubricants are constantly sprayed on its edge, cylinder block liners are still the most essential components of an internal combustion engine, raising concerns about its own reliability and performance. Due to the influence of combustion gas pressure, crankcase pressure, side thrust, and inertial force from the crankshaft, engine friction is an influential area of research in the field of internal combustion engines.(Nagar, 2011) .An ideal cylinder block is shown on figure 1.

In multi cylinder engines, the cylinder will rest in different positions with respect to top dead centre and bottom dead centre subjected to air fuel mixture and engine oil at the same time. If the engine is rested without operation for a long period of time surface reaction occurs which can deteriorate the engine characteristics by a faster catalytic reaction. Corrosion of the cylinder block liner is shown in figure 2.

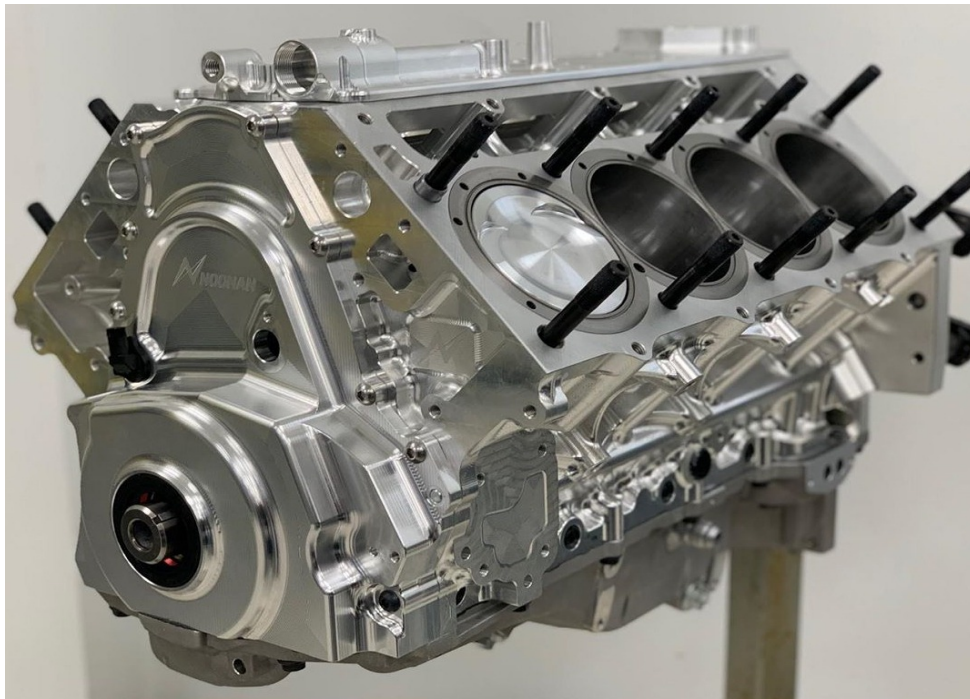


Figure 1: LT4 V8 engine block

Corrosion can lead to surface irregularities which contribute towards atmospheric pollution by transferring vapourised crankcase gases and volatile chemicals to escape to top dead centre which later on passes through exhaust stroke. Meanwhile volatile fuel can enter crankcase leading to blending with engine oil affecting lubricate performance.

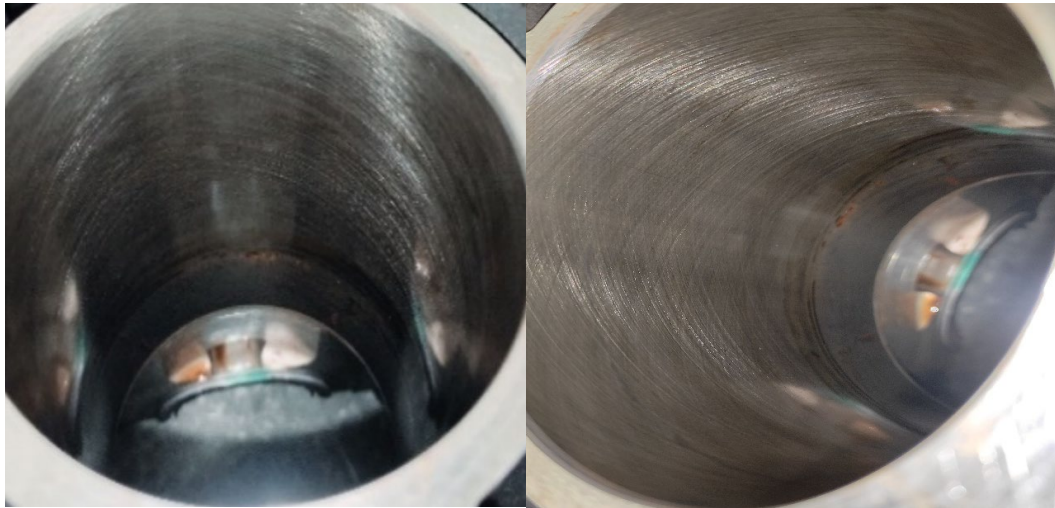


Figure 2: Dismantled view of cylinder block assembly and corroded surface at bottom dead centre (BDC)

The ideal cylinder liner is defined as (dimkovski, 2006) the one that easily adjusts the clearance off the running surface to reduce friction. Minimize high pressure zones and to share wear evenly along the surface by sealing action throughout the operation with Grooves to hold lubricant and collect debris.

Due to erosion and corrosion caused by cavitation, the performance of the system is adversely affected. Cavitation-generated bubble explosions were observed to cause a high level of erosion on the surface of nitride-treated cylinder liners because the surface-treated part was weakly resistant to impact from the blow-up. (Kim, 2021)

2.2 Automotive lubricants and its effects

Engine oil is used in all internal combustion engines and mechanical systems to prevent component corrosion and abrasive wear associated with prolonged contact. (Mohsen Tahmasebi Sulgani, 2019). Friction, is a prevalent energy loss concern in standard combustion engines and several other industrial processes, and it impedes such mechanisms by generating excess heat, which must therefore be removed via cooling systems, resulting in a significant net power loss. (Royal Society of Chemistry, 2018). Lubricants in automotive applications control friction as a function of heat transfer by limiting frictional losses in the surface of mechanical components via boundary lubrication or hydrodynamic lubrication, which signifies the lubricant's molecular attraction (K. Lee, 2009). Since a large quantity of chemicals is being added to base oil to improve the characteristics of lubricant, additives play a significant contribution towards cylinder component wear and tear. Surface treatment with superior surface finish in microscopic approach is essential to ensure the reliability of the powerplant in a lifelong operation.

Degradation of oil during operation have played a significant role in corrosion. Total Base Number (TBN), is a property that measures oil's ability to neutralize acids formed during engine operation. Generally, oils with a higher TBN better neutralize acids and combustion by-products, resulting in longer oil life and improved protection against corrosion. TBN is just one of many engine oil parameters important to engine durability and extended service intervals. The most common causes for a TBN drop are oil oxidation and low-quality fuel with high levels of sulphur. Oil oxidation occurs naturally over time and can commonly be observed in extended drain interval situations. It is also

related to operating temperatures; oils exposed to higher operating temperatures, especially engine overheating, oxidize more quickly. Low-quality fuel with higher sulphur content also depletes TBN. Sulfuric acid formed during the combustion process is neutralized, leading to a corresponding drop in TBN. (United lubricants, 2020). According to figure 2, during phase 3 TAN value increases with respect to TBN concentration of lubricant.

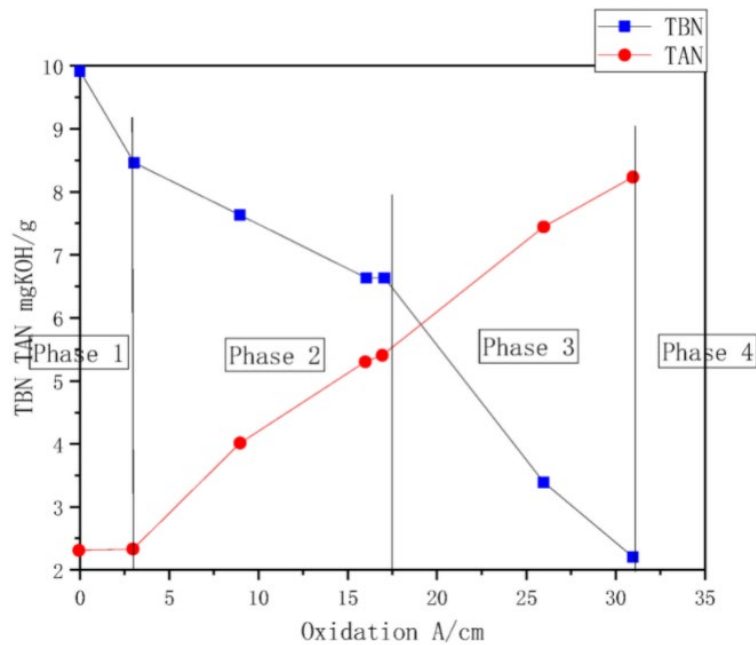


Figure 3: Total Base Number vs Total Acid Number in operating hours (Hao Sun, 2021)

TAN Oil analysis is crucial to maintaining the mechanical integrity of equipment and to prevent internal damage within the sliding components. An oil's TAN will increase with the passage of time or if exposed to high running temperatures where the oil becomes oxidised (during high temperatures, oil molecules react with the oxygen molecules within the air). Oxidation has a significant impact on an oil's ability to protect internal components and can directly affect viscosity. (OCLS, 2020)

2.3 Automotive Fuels and its effects

In a fuel system, fuel is stored, supplied, and burned to produce energy by chemically reacting with air, vaporizing, and being mixed with fuel in the cylinder chamber. Fuel from the fuel tank is extracted from the fuel tank and carried through fuel lines to fuel filters, Fuel pump and finally to either a carburettor or fuel injector, where the combustion process takes place in the cylinder combustion chamber. (Assosiation, 2011). Automotive fuel consists of more than 150 chemical compounds with contribution of benzene, toluene, xylene and lead. The actual composition of chemical compounds keeps varying with the source of the crude petroleum, the manufacturer, and the time of year. (ATSDR, 2014) It is generally believed that gasoline engines are subject to corrosion due to the formation of sulphuric acid from sulphur in low -grade fuels and oils, which is produced during combustion.

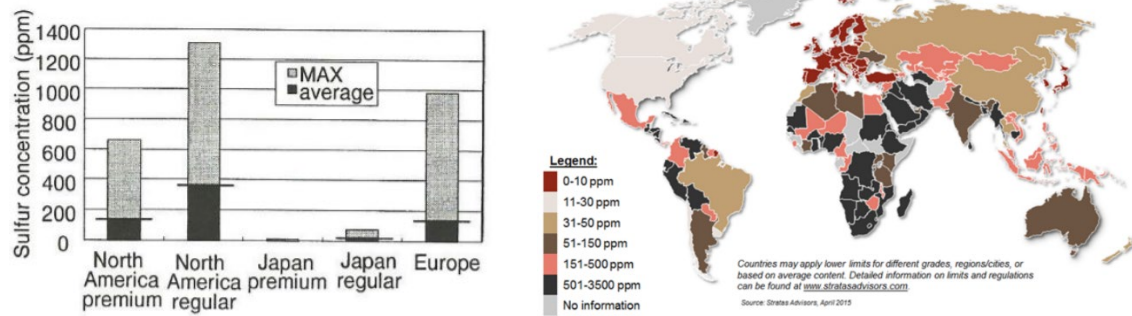


Figure 4: Sulphur concentration in unleaded fuel (Takami Toshihiro, Toyota Motor Corp. Masago Yamamoto, Toyota Central Research and Development Labs, 2000) vs Global Maximum sulphur limit (Stratas Advisors, 2015)

During cold start conditions in coldest countries, condensation of water takes place on the insides of the cylinders and crankcase when an engine is started. The corrosive action of the water destroys the oil-film and comes into direct contact with the metal of the pistons, cylinders, and other parts of the engine, causing them to rust, which later on is likely to result in scored cylinders and pistons. The engine's lubrication system may not be able to supply enough oil to the surfaces, or if the engine is not warmed up properly, condensation and rust can occur rapidly, resulting in excessive wear. (JARDINE.F, 1925). The damage also depends on the surface being attacked and the part being affected. The components under threat are cylinders, pistons rings, valves, valve guides, camshaft, and lifters. (Aviationpros, 2002). Sulphur in fuel is reduced to a greater proportion in the last decade but is still questioned in polluted countries where low grade fuel are used compromising on the environment impact.

3. Aluminium Silicon (Al-Si) Alloy

Aluminium alloys with Si as the major alloying element form a superior class of material providing the most significant part of all casting manufactured materials. In the automotive and aerospace industries, these alloys have a wide range of applications due to the excellent combination of castability and mechanical properties, as well as corrosion resistance and wear resistance. The addition of Cu and Mg to minor alloy compositions improves the mechanical properties (Zamani, 2015) of the alloy and makes it heat treatable. Al-12 Si (EN AC-44300) and Al-Si-Cu-Mg (EN AC-46000) are the most commonly used alloy for casting of cylinder blocks. Chemical composition of metals used in automotive aluminium casting alloys is as follows.

Si	Cu	Mg	Fe	Mn	Ti	Sr	Zr
7-8	3-4	0.25-0.35	0.0-0.4	0.5	0.00-0.25	trace	0.25

Table 1 :Chemical composition of aluminium silicate alloy (wt%) (Bhadeshia, n.d.)

In the past decade, automotive manufacturers have transformed from cast iron to aluminium cylinder blocks for reduction of weight of the powerplant. It has been noted that for gasoline engines, replacing cast iron with aluminium for cylinder block assembly has the potential for an efficient reduction, up to 45% of block weight (Grosselle, 2009) . A disadvantage of using aluminium for cylinder block material is that traditional aluminium alloys do not have the required tribological properties for use as cylinder block material. The use of aluminium cylinder blocks has therefore evolved towards the development of surface engineering technologies that can overcome friction, wear and lubrication. (Lenny, 2011)

3.1 Background of Al-Si Casting alloy

Considering the impact of internal combustion engines on the environment, change in components with respect to thermodynamic property of material led to weight reduction and pollution control. The carbon dioxide emissions and poisonous nitrogen dioxide, trioxide pollutants during operation have reduced to a great extent by improvising the heat transfer characteristics of the powerplant. During manufacturing of aluminium silicate alloys, copper and manganese is added to improve the structural integrity of the block. This helps the powerplant to operate in elevated temperature.

According to the microstructure of aluminium alloys, the alpha-aluminium dendrites contribute the most with respect to eutectic silicon particles, manganese, and copper composition. The size, morphology and distribution of microstructural features govern the mechanical properties of these alloys (J. Olofsson, 2014). The refined microstructure increases the tensile properties of material which is achieved by higher cooling rate.

The most important alloying element in aluminium silicate is silicon. Silicon contributes within 5-12 wt% in a hypoeutectic alloy. Silicon concentration is solely responsible for fluidity in cylinder liners and good castability without cracking during solidifying of alloy. As the Si concentration increases the thermal expansion coefficient decreases also resulting in decreased wear characteristics. Other metals are being added to the alloy to improve the heat treatment and strength. Si content in Al-Si based cast alloys influences tensile properties at both room and elevated temperature, while its role becomes more highlighted in the absence of alloy elements like Cu, Mg, Fe. (F. Stadler, 2012)

Al-Si cast alloys have been alloyed with Cu and Mg for several years to increase their strength at room temperature and elevated temperatures (up to 190 Degree C) as well as their ability to be heat treated. The addition of Mg is associated with enhancing the tensile properties of Al-Si alloys at elevated temperature (up to 200 °C). The presence of Mg also enhances creep resistance and decreases the rate of strength loss at high temperature in the alloys (F. Stadler, 2012) (L. Wang, 1995).

3.2 Solidification of alloy

Al-Si alloys solidify by a primary precipitation of dendrites; an illustration of primary aluminium dendrite (α -Al) structure embedded in Al-Si eutectic is shown in Figure 4. For cubic structures, dendrites often have four secondary arms growing around the primary stem at each junction. (Z.Y. Liu, 2007). The amount of undercooling depends on a variety of factors, including the cooling rate, the concentration and type of the alloying element. As cooling rate increases and alloying element concentration increases, undercooling increases. (H. Fredriksson, 2012)

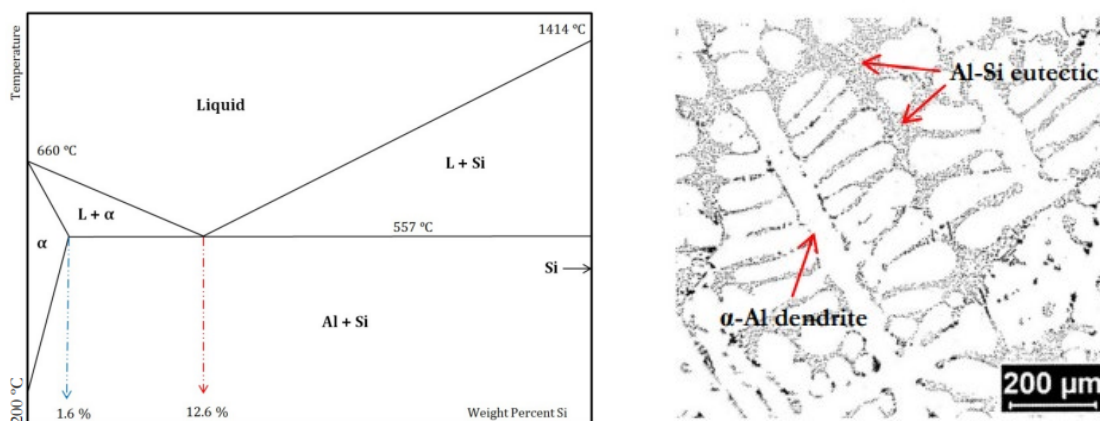


Figure 5: Phase diagram of Al-Si and solidification structure of hypoeutectic Al-Si alloy (E. Sjölander, 2010)

The solidification of the alloy continues with formation of Al-Si eutectic mixture which outlines the perfectly aligned molecules with structural integrity. The liquid and the solid state solidify at the same time during eutectic solidification. (H. Fredriksson, 2012) (Stefanescu, 2002) Figure 4 presents a phase diagram of the Al-Si system with a eutectic point at 12.6 wt. % Si and the corresponding eutectic temperature is 577 °C. Aluminium dissolves a maximum of 1.6 wt. % of Si whereas the solubility of Al in Si is almost zero. Eutectic alloys provide a natural composite which gives good properties for the alloy. Commercial aluminium alloys often contain other alloying elements such as Cu and Mg in addition to Si. The eutectics of these alloys may be more complex than those observed when looking at the binary system. Formation of Cu- and Mg-bearing intermetallic phases often occurs after eutectic formation. (H. Fredriksson, 2012)

4. Determination of Wear characteristics of an Al-Si alloy by experimental analysis

4.1 Tribometer test

In order to understand the wear characteristics of different material, the commonly used cylinder block materials shown in Table 2 are tested to understand the effectiveness of Al-Si cylinder liner over its efficient lightweight, controlled pollution and corrosion resistance characteristics.

For tribological test, cast iron cylinder liners, liners with an iron-based coating (Fe-coated cylinder liners), and Al-Si cylinder liners were all run against nitride steel (nSt) piston rings. The Fe-coated cylinder material was also tested against chromium nitride-coated piston rings (referred to as CrN rings in the following), and the AlSi cylinder material was tested against DLC-coated piston rings acting as the counteracting body. The tribological test analysis was conducted in the test parameters as shown in table 3. All samples were cut from original engine parts, and all material combinations were evaluated with their unaltered, original surface topography. All experiments used standard SAE 5W30 fully formulated engine oil as lubricant.

Cylinder material	Piston ring material
Cast iron (CI)	Nitrided steel (nSt)
Fe-coating (Fe-c)	Nitrided steel (nSt)
Fe-coating (Fe-c)	Chromium nitride coating (CrN)
AlSi	Nitrided steel (nSt)
AlSi	DLC coating

Table 2 : Material combination used for tribometer test

Initial pre-load for 30 s (N)	50
Normal load (N)	100
Oscillating frequency (Hz)	50
Stroke (mm)	1.5
Oil and sample temperature (°C)	120
Test duration (min)	300

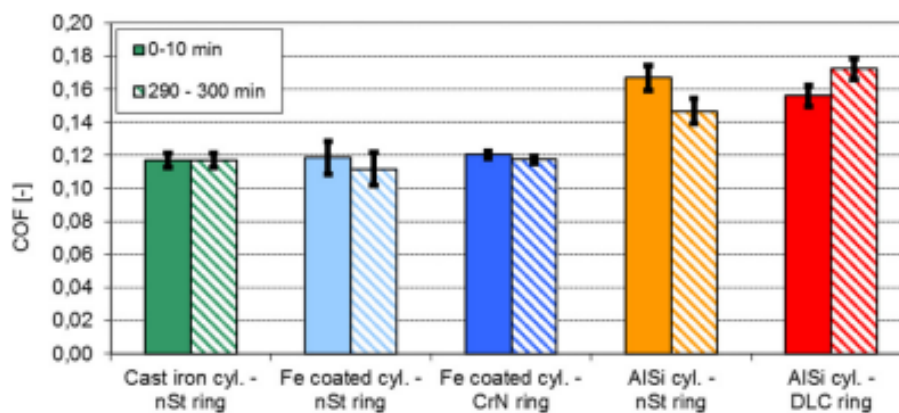
Table 3 : Tribometer Test parameters

4.2 Wear measurement and Results

During tribological test, differential surface topography radioactive isotope concentration (RIC) method was used to continuously measure wear, including running-in and steady-state wear (Jech, 2012). Radioactive tracer isotopes were produced within a thin surface layer of the cylinder samples at the designated contact zone to determine the amount of wear of the cylinder liner materials.

4.2.1 Coefficient of friction

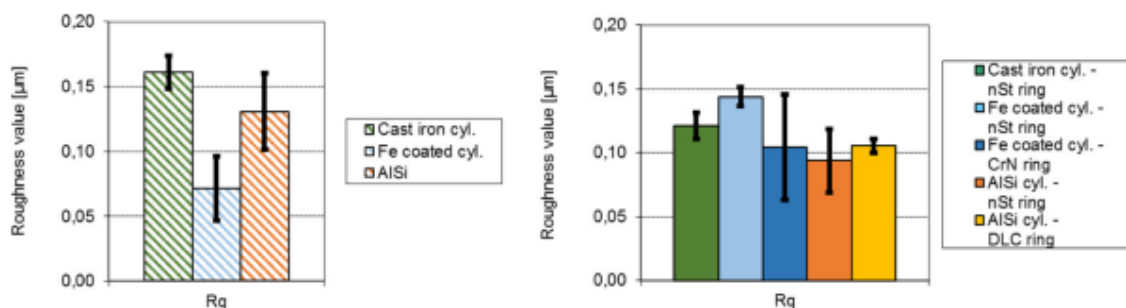
From graph 1 obtained from the coefficient of friction during tribological test, the average friction coefficient of material pairing for the first and last 10 minutes of the test is taken into analysis. The material pairings with the Al-Si cylinder liner show higher friction coefficients than the other material pairings of cast iron. The piston ring with nitrided steel ensured less coefficient of friction in the 290 to 300 minutes of operation whereas piston rings with DLC coating increased the frictional losses during the test



Graph 1 : Coefficient of friction of different cylinder block liner and piston ring material combination with mean values of first and last 10 minutes of tribometer test. (Wopelka, 2018)

As the coefficient of friction increases, wear characteristics increases resulting the material degradation with respect to operating conditions, not recommended for the operation as reliability of a powerplant is quite a concern.

4.2.2 Roughness



Graph 2 : Roughness characteristics of different material pairing before(left) and after(right) the tribological test (Wopelka, 2018)

As in graph 2, Before the wear test the Fe-coated cylinder material have the lowest initial Roughness. The initial Roughness values of the cast iron cylinders are slightly higher than the Al-Si cylinder roughness values. After the wear test as in graph 2, the Roughness values of the cast iron and Al-Si

cylinders are lower than those before the test, whereas the Roughness values of the Fe-coated samples are higher than those before the tribological test.

As the surface characteristics of aluminium silicate have disadvantages over its lightweight, corrosion resistance characteristics due to roughness and friction coefficient, the Al-Si alloy combination is not recommended for cylinder block liner material where it can be used as material for cylinder block assembly. Twin wire arc spraying of the liner is done to improve the substrate surface characteristics to make it best suitable for the application of internal combustion engines.

5. Surface Treatment of the substrate

5.1 Twin Wire arc spraying

After decades of development of the internal combustion engines, there is a widespread attention in the development of powerplants with respect to carbon dioxide reduction, reliability and improved fuel economy. The twin wire arc spraying process of surface treatment of aluminium cylinder block liners creates a thin alloy coating with combination of iron and carbon, which is later on surface finished by the process of honing. Mercedes Benz generated Nanoslide technology during 2009 which changed the revolution of high-performance cars where twin wire arc spraying method is used to melt the iron and carbon wires, spraying them to the walls of aluminium cylinder wall with help of gas flow. The twin wire arc spraying of aluminium cylinder liners processed by Daimlers Nanoslide technology is shown in figure 5.

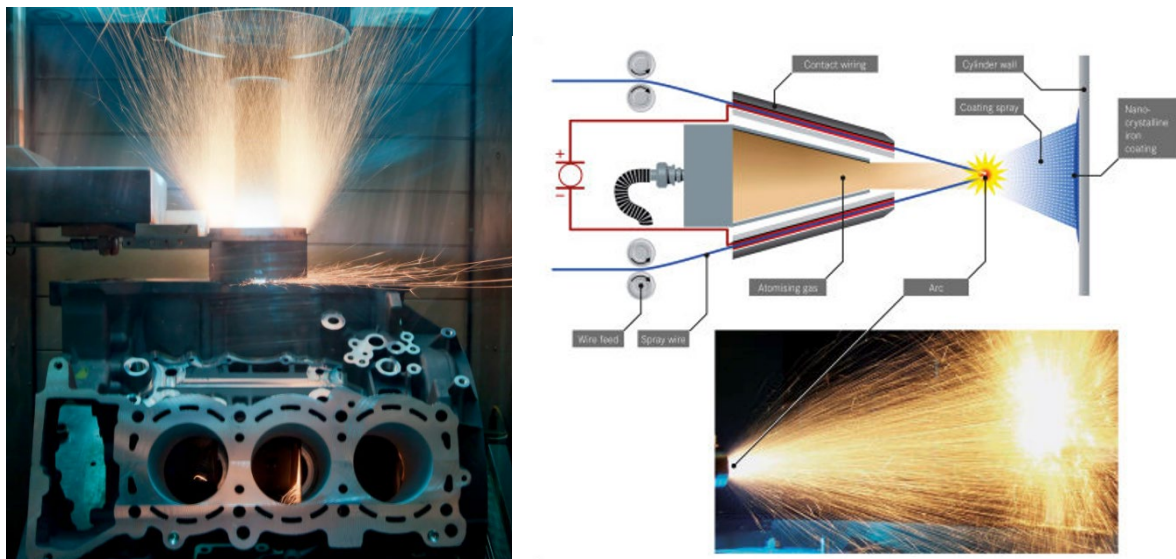


Figure 6: Daimlers Nanoslide twin wire arc spraying process of cylinder block liner (DAIMLER, 2011)

The process of twin wire arc spraying method is described in figure 5. The torch's primary element is patented wire and gas direction. The wire material and the process gas are induced axially to the torch's rotation axes. The rotation axis is perpendicular to the cylinder's central axis. The outlet direction of the two wires has both a radial and an aligned direction. The advantage is that the arc is always positioned in the gas jet, even though the wire supply constantly changes. This allows for a spraying angle that is orthogonal to the substrate (D. Nowotni, 2002).

Spray Wires of iron and carbon is passed through separated wire field directed towards arc where one of the elements is connected to positive terminal and negative terminal respectively. Atomising gas is sprayed between two melted wires resulting in generation of an arc at point of contact of these two

wires resulting in a combination of coating spray which is directed towards the cylinder wall resulting in the formation of nano crystalline iron coating. Final finishing of the resulting, layered ultra-fine nano-crystalline iron coating creates an almost mirror-like surface with fine pores on cylinder wall achieved by mechanical honing.

5.2 Mechanical Honing

Development of high-quality mechanical components by manufacturing includes mechanical honing, which is a common manufacturing process by which surface finish is being obtained by abrasive treatment against the walls of the substrate coating with a tool made of rotary abrasive stone. The honing tool consists of a rotary shaft rotating on a spindle with abrasive stones mounted on a suspension. The honing process is shown in figure 6.

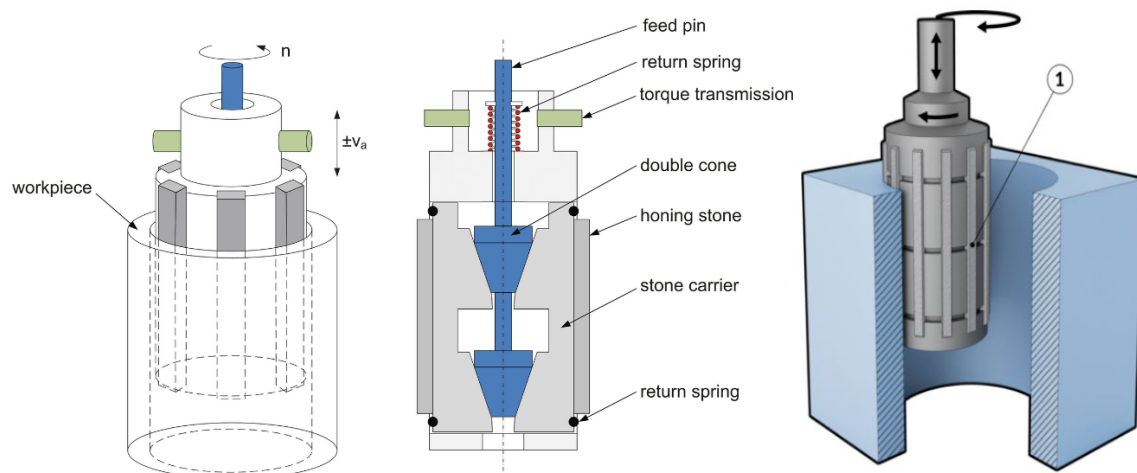


Figure 7: Surface finish of cylinder block liner by mechanical Honing method (Hoffmeister, 2019)

During honing of a cylinder block, the tool is inserted into the workpiece with the help of suspension spring. The tool oscillates axially and moves in a circular motion while grinding, rubbing against the hole wall. A cutting fluid cools the tool and washes away any formed swarf (Manufacturing Guide, n.d.). Feed pin rotates the tool at n revolutions per second which is strongly dependant on the type of material inside cylinder block liner. Honing serves to improve the shape, size, subsurface, and surface quality of the cylinder block liner as shown in figure 7.

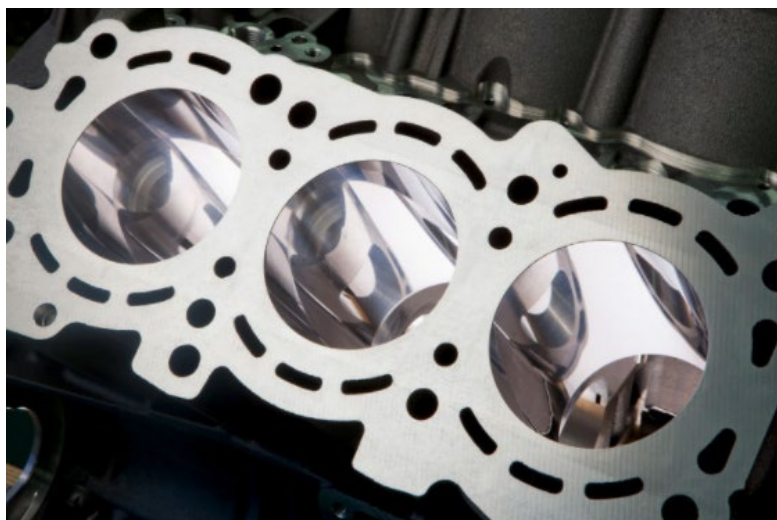


Figure 8: Cylinder block liner surface after mechanical honing process (DAIMLER, 2011)

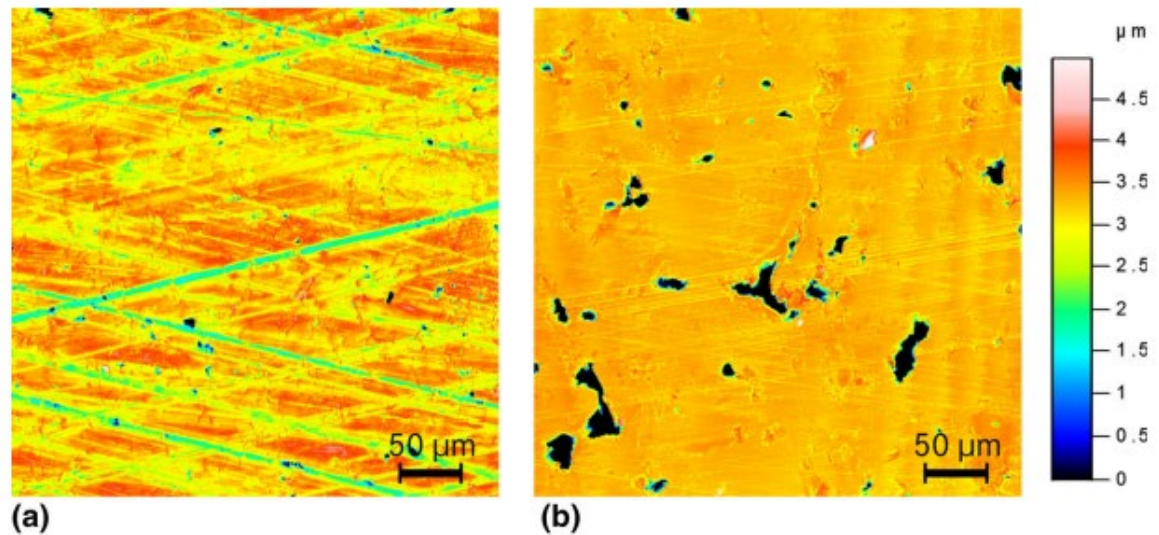


Figure 9: Honing surface of (a) Gray cast liner (b) Nanoslide cylinder liner (Johannes König, 2014)

The objective of this process is to create a distinctive bore with a generous, smooth surface that is resistant to corrosion and enzymatic attack. This surface structure reduces friction and allows for adequate lubrication properties. Unlike traditional liner technology, no typical honing structures were embedded Fig. 8(a). Furthermore, the typical pore structure of the Thermal wire arc sprayed liner coating is disclosed, which adapts to an appropriate oil detention volume with excellent surface characteristics in a microscopic approach Fig. 8(b) (Johannes König, 2014).

6.Conclusions

The research and development of aluminium alloys as the cylinder block material of internal combustion engine keeps evolving due to their lighter weight at the expense of strength, hardness, and resistance to corrosion. Using of lighter weight materials in manufacturing of powerplants helps emission control resulting in energy efficient and clean operation:

Cylinder block liners need more attention on an internal combustion engine due to the action of chemicals acting as a catalyst to enzymatic reactions due to following reasons

- With regards to resting and initial warmup of a powerplant, Cylinder block liners requires extensive substrate protection initially the most from the reaction of sulphur in automotive fuel, vapourised phosphorous in lubricants and hundreds of other chemicals present in their composition.
- TAN (Total Acid Number) in lubricants increases with operating hours of an engine. Monitoring of the engine oil degradation is essential where TBN (Total base number) value of an engine oil protects the acidic reaction of lubricant on cylinder components.

With silicon, manganese, copper and zinc as alloying elements in Al-12 Si (EN AC-44300) and Al-Si-Cu-Mg (EN AC-46000) (Zamani, 2015) the wear properties of the Al-Si block as cylinder liners were investigated using tribological test of 300 operating hours to calculate surface topography (Wopelka, 2018). The following results are found with a methodology to generate new surface characteristics.

- Higher wear characteristics on Al-Si alloy cylinder liner is noted where Structural integrity of the material and wear measurement is considered vital parameters for the application.
- Surface treatment of the substrate by Twin wire arc spraying (TWAS) is done to add a thin layer of iron and carbon coating at elevated temperature to meet the requirements of a cylinder block liner.
- Mechanical honing is done as a process of surface finish to generate a smooth surface where surface quality of a cylinder block liner is achieved for efficient operation.

As a result of a Twin wire arc spraying methodology combined with mechanical honing to improve the substrate surface finish, an efficient stoichiometric combustion capability will control emissions with efficient action against chemicals in fuels. The degrading parameters of lubricants are controlled by fluidity of the liners where monitoring engine oil degradation can help the user for extensive reliability of Piston ring and cylinder block liner. The lightweight character of aluminium silicate alloys plays a significant role in structural integrity with strong material bond in core structure resisting environmental degradation parameters.

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