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Nanocoatings for engine application

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Abstract

In this paper, a review of engineering coating for engine application is presented. Issues relating to dimensional stability, tribological properties, lubrication, coefficient of friction, hot hardness, amenability for honing, surface roughness and topography, residual stress, adherence, damage tolerance and resistance, pores density and conditions and cost performance are discussed. There exist advantages and limitations of conventional materials systems and techniques such as chemical-vapor-deposited diamond-like carbon (DLC) coating, plasma sprayed metal matrix composite coating, tribologically functional ceramic coatings, etc. Nano-grains of a crystalline phase hold promise to solve several such problems present in conventional coatings. In addition, surface-related problems are addressed for high performance engines and hydrogen powered automotive engines.

Keywords: Nanocoating; Engine application; DLC

1. Introduction

Depleting fossil fuel resources, economic competitiveness and environmental concerns has compelled to explore newer avenues to improve efficiency of automotive engines. Various techniques have been adapted to achieve this goal. By allowing the engine to operate at higher temperature with reduced external cooling (heat removal), the fuel efficiency can be improved significantly. There is a need to address several materials related issues such as thermal distortion, high temperature oxidation, creep, etc. Other methods to improve fuel efficiency are to use lightweight material to reduce load, reduce heat losses due to exhaust and conduction through engine body and to reduce frictional losses. Reduction in the weight of engines is a key factor in improving the fuel efficiency. The use of lightweight materials has become more prevalent as car manufacturers strive to reduce vehicle weight in order to improve performance, lower fuel and oil consumption, and to reduce emissions [1]. Most manufacturers have replaced cast iron (density = 7.8 g/cm^3) engine blocks with lightweight and low-cost aluminum-silicon (density = 2.79 g/cm^3) crankcases. Several Al-based alloys and metal-matrix composites, such as A319Al, A356Al, A390Al and A360Al, are in use. However, inadequate wear resistance and low seizure loads have prevented their direct usage in the cylinder bores. The cylinder bores of these aluminum alloy blocks are usually made of cast iron liners because of their good operating characteristics such as wear resistance. These liners need to have a specific wall thickness, which results in a relatively large web width between the individual cylinder-bores, and increases the dimensions and weight of the engine. Moreover, mechanical friction is of another concern that needs to be addressed. Piston system is a major contributor to engine friction [2]. The cylinder bore/piston and piston ring friction constitute nearly all of the piston system's friction losses [2]. A major portion of oil consumption arises from bore distortion and poor piston ring sealing resulting from ring and bore wear. Aluminum exhibits a transition from mild to severe wear when the nominal contact stress exceeds a threshold value [3]. Presence of reinforcement particles does prevent such transition until higher threshold values. Such a situation can arise due to following factors: (1) start of ignition where oil has not spread over entire surface; (2) bore distortion. Thus, to continue using aluminum alloy engine blocks (due to lighter weight) and to improve wear resistance of the engine bore surface several techniques have been explored.

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These techniques are dedicated to form new composite and/or monolithic coating on the bore surface, such as, use of atmosphere plasma sprayed coating (APS) [4,5], high velocity oxy-fuel (HVOF) coating [5,6] and use of costlier and harder substrate materials [7,8], etc. However, in case of automotive engine by obviating the need for liners, the engine dimension can be significantly reduced. It is estimated that direct weight savings of about 1 kg per engine can be easily achieved [8,9]. Also, elimination of liners allows reduction in the overall dimension of engine [5,8,9]. Every kilogram reduction of payload is important for improvement in fuel efficiency. Reduction of about 110 kg in a typical automobile of weight 1100 kg will improve fuel economy by 7% [10]. In the lifetime of a car this reduction of engine weight is significant. Application of newer technology and/or materials is being explored to achieve this goal. By employing nanomaterial much of this objective can be achieved. Nanoscale materials have received much attention in recent years due to their outstanding properties compared to those of micron-size counterparts. The nano-world possess so much potential that Nobel laureate Dr. Richard Smalley envisions deploying nanotechnology to solve the energy problem of the tomorrow's world [11]. Employment of nanotechnology in current and future automotive, aero and other engines will go long way in solving energy crisis.

The defect density in nanoscale materials is very high, but not high enough as in amorphous. As depicted in Fig. 1, Hall–Petch relation (Hardness for a polycrystal with average grain diameter d, H_d = Hardness of single crystal, $H_0 + kd^{-1/2}$) predicts increase of hardness and flow stress as the grain size decreases. However, as the grain size is very small (in the range of 100 nm), the deformation mechanism changes from dislocation controlled slip to grain boundary sliding increasing plasticity at the same time. When the grain size further reduces almost to become amorphous, the material behaves in visco-elastic manner. This provides a global maximum in properties such as hardness, flow stress, toughness, ductility and thermal insulation (because the conductivity of nanoscale material is much less in certain metallic system such as aluminum due to phonon scattering by high defect density) when the grain size is in nanoscale. It is, therefore, envisioned to apply nanocoating to solve the imminent problems in engines for various applications. Understanding of the general coating characteristics is necessary and is presented herein.

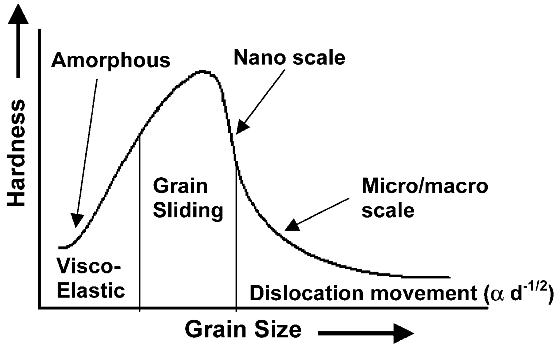

Fig. 1. Schematic depiction of hardness as a function of grain size.

2. Desired characteristics of engine coating

Coatings, particularly nanocoating can help to improve performance and life of automotive engine. Higher efficiency is realized from various aspects of coatings as schematically presented in Fig. 2. In this section, desired characteristics of coatings are discussed briefly.

2.1. Coating with good lubrication

It is essential to have least frictional forces present in between mating and/or reciprocating components. High coefficient of friction leads to higher wear rate affecting the engine life. Besides, mechanical friction has significant effect on the internal combustion (IC) engine fuel economy [2]. In an IC engine, the major sources of frictions are valve train, piston system, crank and bearing system. Mechanical friction represents 10–15% of Indicated Mean Effective Pressure (roughly translates into energy available in a combustion cycle). Of the total frictional loss about 50–65% is accounted for in piston system alone. Valve train system (tappet/cam journal) contributes 10–20% of friction loss and crank and bearing contributing the rest [2,9]. There is a pressing need to reduce these frictional losses to improve overall efficiency of the engine, reduce oil consumption and to increase life of engine. Various coatings being considered for this purpose are Ni–Mo–MoS_2, Ni–BN, graphite–Ni, etc.

2.2. Corrosion resistance

Engine components are subjected to severe environmental stimuli for corrosion. The higher temperature, fuel and combustion products mixed with oxidizing atmosphere and thermal shock add to the corrosive media. Diesel engine and internal combustion (IC) engine even produces sulfuric and formic acid as a product of combustion under certain conditions such as cold weather. Coating, especially Mo/Cr based, are most suitable to combat elevated temperature corrosion in such environment.

2.3. Tribology properties

A coating is applied to improve the wear resistance and scuffing resistance at least as good as the cast iron liner they substitute. Fine grained tribologically functional ceramics such as Al_2O_3, SiC and Fe-oxides present in a coating can improve surface related properties such as hardness, compressive strength, abrasion resistance and scuffing resistance [4,7,9]. Scuffing is the major tribological issue defined as

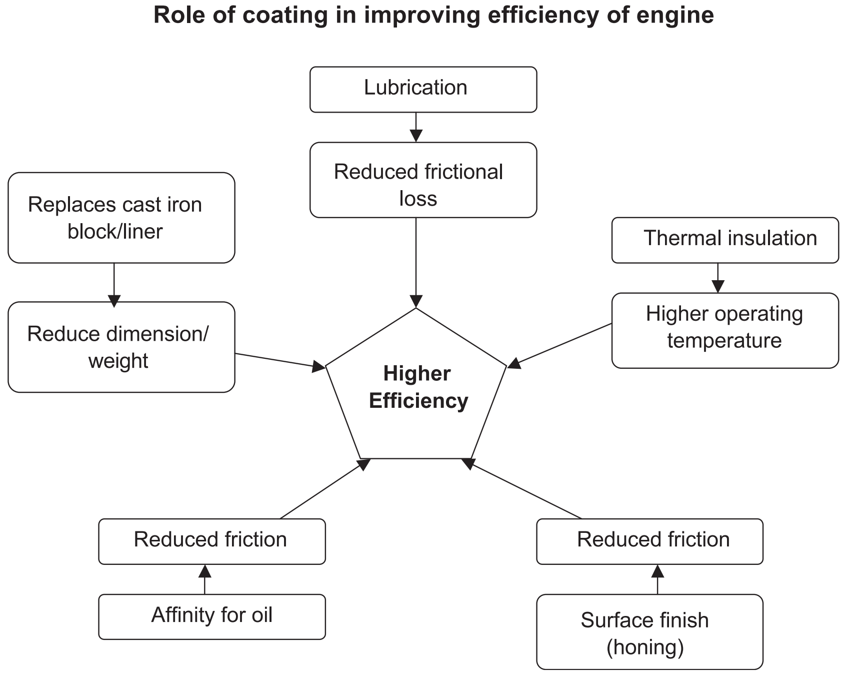

Fig. 2. Role of coating in improving efficiency of engine.

mass movement of surface elements via contact between two metals, especially when lubrication film breaks down [12]. The coatings should also possess good mechanical and thermal shock resistance, good adhesion and strain compliance with the aluminum alloy substrate to meet the engine durability requirements. More details are reported in the later sections.

2.4. Amenability to honing

After the cylinder wall has been coated, a special parallel honing process is used to create a surface topography with numerous small recesses, which serve as oil reservoirs. This leads to an improvement in hydrodynamic lubrication and reduces piston ring stress [13]. Honing is preferred over other surface finishing procedure because of primarily two reasons. Honing gives a suitable topography to keep residual lubricant in the microcavities. Honing, unlike grinding or machining, does not close the pores that act as lubricating oil pockets. Secondly, debris and foreign particles sit in valley of honed surface thereby reducing interference with wear characteristics. Typically surface roughness R_a is maintained below 0.2 μm during honing to minimize wear [4]. A coating material should be amenable to honing. Another issue is the coating thickness should be large enough so that a sufficiently thick coating is left even after honing. This thick coating should be adherent enough so that coating damage (fissures, breaks and spallation) can be prevented during such surface finishing. The coating properties should be consistent and uniform to provide reliability with regard to honing (surface finishing). There must also be sufficient coating thickness to allow correction of the contour deviations or lack of cylindricity that may be present in the component and/or developed during coating operation. The thickness allowance for a tested and stabilized coating process is between 100 and 150 μm in the bore diameter. Compared to the traditional cast iron liner, the specially honed coatings result in 20–30% lower friction [4]. Because of the tribological characteristics of the plasma coating, the life cycle of the engine is lengthened, while emissions decrease as a result of the reduction in fuel and oil consumption. It has been reported that plasma sprayed Fe/FeO as well as stainless steel/BN coatings reduced ring/bore wear by 40% and improved engine oil economy by 13600 km/l [14].

2.5. Heat transfer

Heat transfer to the block is kept to an absolute minimum, since this represents heat loss. The coating should have low thermal conductivity, insulating the combustion chamber from conduction mode of heat transfer through aluminum or super alloy (as in gas turbine). Thermal barrier coating (TBC) was developed with an aim to reduce heat transfer. Computer simulations of internal combustion (IC) [15], diesel [16] and rocket [17] engine as well as experimental data of diesel engine [18] have shown that if the engine cylinder wall is coated externally by 2-mm thin layer of an insulating oxide, the heat loss is reduced by 6%. If a coating is applied on inner diameter of cylinder bore, then the thermal gradient is lower for conduction mode heat transfer and the heat loss is further reduced.

2.6. Strong affinity of coating for oil

For better lubrication and lower friction loss, it is desirable to operate the engine in hydrodynamic regime of friction [2,4]. A breakage of oil film often leads the engine to operate in boundary friction regime (metal-to-metal contact) or mixed mode [19]. The coefficient of friction in this regime is very high compared to hydrodynamic regime; hence, higher wear is encountered. It is essential that the coating should have great affinity for lubricating oil. Then, in case of occasional breakage of the film, oil can move in through honed textures (capillary action) to repair the film-breakage and bring back to hydrodynamic friction regime (film rupture strength of engine lubricating oils 1.5–5 GPa for IC engines [20]).

2.7. Adherence with substrate and thickness of coating

Good adherence with the substrate is a must to achieve a coating that exhibits resistance to thermal shock as encountered in engine application. Bond strength in Atmospheric Plasma Spray (APS), HVOF and magnetron sputtering coating is a strong function of surface roughness (R_a and R_z) prior to coating and residual stress (a strong function of coating thickness) [21–23]. The maximum coating thickness depends on the heat expansion coefficient and the mechanical properties of the coating. If the heat expansion varies too much in the base material or if the elasticity or ductility is too low, a coating that is too thick may not adhere correctly due to internal stress. On the other hand, a residual coating thickness of 100 to 180 μm must remain after honing in order to effectively cover any casting pores in the base material [4].

Thermal cycle during application of the coating to Al–Si substrate (both hypo- and hyper-eutectic) should consider the fact that this eutectic system can undergo distortion or metallurgical change in microstructure. It also should be taken into consideration that most cylinder bores have inner radius of 70–110 mm and such dimensions call for special tooling for applying the coating.

In a thermal barrier coating (TBC), a bond layer is applied above nickel-based super-alloy to improve the adherence of oxide coating. The thermally grown oxide, has good coherency with the bond layer, on which another oxide layer (zirconia or titania–alumina) is plasma coated. The oxide layers also act as insulating resulting in minimum heat loss due to conduction.

2.8. Meeting the high-quality requirement

The cylinder bore, piston ring and lubricant interact as a tribological system in the combustion engine. The main challenge of an industrial solution for the coating of cylinder bores is not only to develop a suitable material and process, but also to integrate that process into a cost effective, high volume, fully automated production coating system.

This coating machine must be capable of meeting the stringent quality requirements of the engine manufacturer. The coating system not only controls the coating process, but also the surface preparation, cleaning, cooling and transportation of the engine blocks through the system. Also, the coatings of the piston system need to be considered as a whole to prevent induced wear. For example, extremely hard piston can cause wear in the liner.

2.9. Excellent price/performance ratio

The typical cylinder diameters of 70–100 mm necessitate a short spraying distance. Also, the process has to be very flexible because of the frequent changes in design, manufacturing process and geo-politico-commercial factors that affect auto industry. In comparison to other techniques, plasma spraying fulfills these requirements better [4,5,8,9]. It distinguishes itself not only through high flexibility in the casting process with which the engine blocks can be manufactured, but also with its excellent price/performance ratio. In comparison with other coating processes for cylinder bores, such as nickel dispersion coatings, HVOF and electric arc wire spraying, plasma is less expensive and more efficient. The coating should be economical and cost effective and should not be based on strategic materials such as cobalt or nickel.

Atmospheric plasma spray coating is in use at several auto manufacturers. Also, APS is extensively used for thermal barrier coating of nickel based super alloys component of aero and gas turbine engine components [24]. However, materials issues such as adherence to substrate, porosity, residual stress particularly for thick coating, etc., have left a lot of room for improvements.

3. Coatings for engine and other automotive power systems

Cr electroplating is regularly employed to coat the piston rings in engine. Different types of ferrous-based powders, containing C, Si, Sn, Ni, Cr, Mo, Cu, Ti, V and B, etc., are also employed to coat Al alloys for diesel engine applications. APS and Laser Surface Engineering (LSE) have been explored for such coatings [4,5,8,9]. Since diesel engines are exposed to sulfur containing material, corrosion resistance in sulfuric acid is a standard test for such a coating and usually contains aluminide or Mo/Cr in ferrous base coatings [24,25].

Nickel–chromium/chromium carbide coating on piston rings applied through both APS and HVOF techniques have shown potential for improvements on the basis of engine tests. Plasma-sprayed chromium oxide shown to perform better than other coatings in high horsepower diesel engine [6].

Thermal barrier coatings (TBCs) (usually zirconia or alumina–titania) were traditionally applied to gas turbines blades and vanes in order to reduce their operating temperatures and/or increase component durability. TBCs can improve engine efficiency by increasing the working temperature and/or reduce heat loss through the components. Zirconia happens to be the material of choice for overlay because of its low thermal conductivity (~ 1 W/m^2 K) and high coefficient of thermal expansion (CTE) (6×10^{-6} m/m/°C) combined with minimal temperature sensitivity and proper chemical stability at high temperature [26,27]. Furthermore, ceramics, such as zirconia, exhibit excellent wear characteristics as well. Yttria stabilized zirconia (YSZ) has a thermal conductivity an order of magnitude below that of Ni-based super alloys, whereas the coefficient of thermal expansion is close to that of Ni-based substrate. YSZ based coating has been successfully applied on IC engine piston crowns as well [18].

In the present gasoline automotive engines, it is often possible to coat cylinder bore with solid lubricating materials that can reduce friction and thereby wear. Metal powder encapsulated solid lubricants can be used for bore coating in auto industry using atmospheric plasma spray [4,5,8,9,14,23,28]. Also, the friction coefficient decreases as the temperature increases for solid film lubricant (SFL). An additional advantage of using solid film lubricant is to reduce formic acid corrosion attack during extremely cold weather, occurring with methanol-based fuels.

Nickel free solid film lubricants usually containing fluorides, CaF_2 and BaF_2, which (instead of Ni–BN) can reduce and stabilize the coefficient of friction of Cr_2O_3 coating. This will further improve tribological properties of chromium oxide (Cr_2O_3) coating for engine applications [4,5]. Stainless steel and nickel encapsulated hexagonal boron nitride (BN) and the one with iron and its oxide (Fe–FeO) systems have been extensively studied by auto industry [9]. The Fe–FeO system is aimed at significant cost reductions to make the coatings attractive for general consumer auto engine applications (non-luxury auto models).

A study on the use of graphite as solid lubricant shows that even though there is a significant improvement in the scuffing resistance under normal load, however, at high loads it did not provide adequate resistance to scuffing [7]. Such high contact load is encountered when there is a bore distortion and also in the piston reciprocating area. Also, breakage of lubricating film leading to boundary regime of friction (metal-to-metal contact) can also cause high contact stress [2,9]. It is necessary to improve hardness along with use of solid lubricant to get optimum performance of the coating. The coefficient of friction is correlated with the amount of solid lubricant in contact area. It is therefore desired to improve the distribution of these tribologically functional phases (graphite or fluoride or iron oxide).

Traditionally, the piston rings are chrome-plated for wear resistance. An HVOF coating of cermets has shown potential as an alternative to chrome plating. Coating materials, primarily NiCr/Cr_3C_2 and NiCrMo/Cr_3C_2, have been proposed for high horsepower diesel engines [6,16,18]. Cermets are new coating materials for aeronautical application. Both APS and low pressure plasma spraying (LPPS) are used to coat a bond layer and cermet layer on directionally solidified (DS) Mar-M246 + Hf super alloys and Ni_3Al based IC6 super alloy [29,30].

Amorphous carbon or diamond-like carbon (DLC) is well known as a preferred material for tribological applications for high hardness, wear resistance and very low friction when sliding against most engineering materials [31]. Application of DLC as protective coatings for piston rings provide significant benefit in the reduction of friction loss (thus fuel consumption) and increase of working life and reliability of the engine [32]. However, protective coatings should have a certain thickness to ensure a longer working life. Unfortunately, one of the major shortcomings is that the pure DLC has very high internal stress, thereby limiting its thickness [32,33] (Fig. 2).

4. Nanocoatings in engine applications

Design for coatings with an amorphous matrix of DLC and metal nano-grains of a crystalline phase to be embedded in this matrix are being investigated [33]. These coatings have low residual stress, high hardness, and high toughness and exhibit very good tribological properties.

The nano zirconia powder (<50 nm), can be used to coat various substrate by atmospheric plasma spray [29]. Even though there is some degree of grain growth during the plasma spray, usually the nano dimension is retained. Based on Jiang's model of grain growth during non-isothermal annealing, the nanostructure can be sufficiently preserved at elevated temperature, if the heating rate is high enough, as experienced during thermal spraying [34]. It is observed that some degree of grain growth associated with plasma spray is responsible for better consolidation of the coating vis-à-vis melting encountered during high heating rate in plasma spray [29,30]. The nanocoating exhibits higher coefficient of thermal expansion (CTE), lower thermal diffusivity and hysteresis, higher hardness and toughness compared to the traditional (microscale) coating. The lower thermal diffusivity is due to extra phonon scattering by boundary defects. Higher hardness and toughness is the result of small grain size. It is also expected that the nanocoating would exhibit grain-sliding plasticity [35].

Besides DLC and TBC, not much work has been reported in the field of nanomaterials in engine applications, particularly for auto engines. Improved chemical, mechanical and physical properties of nanocoating hold tremendous potential for improvement in auto industry, and current and future power train systems. The superior set of properties of nanoscale materials has the potential to accelerate this transition from a limited fossil fuel to a renewable, virtually unlimited energy source, namely hydrogen. Currently, hydrogen is being considered as the major energy source of the future.

4.1. Hydrogen future

Despite of socio-politico-economic elements involved, it is unlikely that any technology would displace the gasoline fueled IC engine—at least not by 2020 or 2030 because of lack of infrastructure that may take decades to evolve and replace the gasoline technology entirely. Perhaps, diesel or ethanol powered vehicles in conjunction with a hybrid-electric technology seems more likely event [1,36–39]. Besides, gasoline powered light duty vehicles, diesel powered off-road engines such as bulldozer, construction equipment, farming equipment, railroad engine and portable power generators constitute 30% of diesel market. Unfortunately, this sector is one of the largest air polluters [40,41].

Hydrogen is the largest potential renewable source of energy. It is envisioned that the primary source of hydrogen would be catalytic electrolysis of water by photons present in Sunlight. However, the photovoltaic panels remain extremely inefficient owing to very little absorption [11]. The solar panels currently in use are energy inefficient since most of the photons are either reflected back or lost as unusable heat. Nanocoating and modification of the photovoltaic cell surface in nanoscale holds promise to improve the energy efficiency. Moreover, the photons present in visible light are energetic enough to cause hydrolysis-dissociation of hydrogen and oxygen in water. It is, therefore, possible to generate greater amount of usable energy from the solar cells by coating with dye sensitized solar cells based on nanocrystalline oxide semiconductor (TiO_2) and transition metal complexes [42,43]. Several technologies are being explored for generating hydrogen more efficiently. The most popular technology is electrochemical cell using proton exchange membrane fuel cell (PEMFC). Nano materials are being explored for this purpose [43].

A bipolar plate material in proton exchange membrane fuel cell (PEMFC) should have very good wettability, very good electrical conductivity and small contact resistance, high surface activity (catalysis), corrosion resistance (particularly galvanic corrosion) against weakly acidic aqueous medium (sulfate, chlorides ions and O_2 and Hydrogen) [35]. These seemingly conflicting properties pose harder obstacles for design and selection of material for hydrogen fuel cells. Passivated austenitic stainless steel may provide good corrosion resistance but increased contact resistance and possible vulnerability to hydrogen embrittlement have limited its application [37]. A nanocoating can hold promise for a more practical plate material. YSZ, $Cu(In,Ga)(Se,S)_2$, vanadium oxides or ZrO_2 based nanocoating shall improve electrical conductivity and reduce contact resistance, improve wettability and activity [44–46].

It is, therefore, essential to improve the efficiency of all kind of engines. As discussed previously by reducing friction and operating the engine at higher temperature, the efficiency can be drastically improved. The high thermal stresses and the severe wear regimes in the cylinder bore lead to delamination of the coatings with catastrophic failure since plasma coatings are often not metallurgically bonded. Furthermore, it is difficult to get a coating of consistent quality in the case of thermal spraying and these coating requires extensive surface preparation [47,48]. Even though various coating techniques are in use, laser surface engineering of cast Al alloy engine cylinder block is promising. High volume production in automated manufacturing set-up line and formation of metal matrix composite coating via laser surface engineering via melting and resolidification is a feasible technique. Laser induced reaction between iron oxide and aluminum to form a self-propagating high temperature synthesis of nanocoating is being explored and a review on the topic follows.

5. Laser assisted reaction induced nanocoating

The ongoing efforts by the authors to synthesize a laser induced iron oxide reaction coating on aluminum alloy have shown promise in LSE for engine applications. The following section deals with such effort. Objective of this research project is to enhance the surface-related properties of aluminum alloys by synthesis of laser induced reaction nanocomposite coating suitable for auto engine applications. In this study, a popular casting alloy A319Al is chosen. A319Al [5.5–6.5 wt.% Si, 3.0–4.0 wt.% Cu, <0.5 wt.% Mn, <1.0 wt.% Fe, <0.1 wt.% Mg, <1.0 wt.% Zn, <0.25 wt.% Ti, <0.35 wt.% Ni, <0.5 wt.% others (total) and balance Al] is an Al–Si–Cu alloy known for its excellent castability, high strength, good corrosion resistance, and pressure tightness [31]. Even the hard and stiff Si particles that have fallen off the matrix can enhance the wear process by acting as abrasive particles. These Si-rich particles also hinder machining and honing. Hypereutectic alloy A390Al is limited to only luxury cars such as Mercedes and Porsche because of its expensive machining operation [7]. Also, the interfaces between Al and Si-rich phases act as potential site for fatigue crack initiation and propagation. Fortunately, Al–Si binary system is amenable to modification, primarily by depression of eutectic reaction temperature [49,50]. Modification results in extensive refinement of microstructure and morphology can improve mechanical properties to a great extent. Addition of Sr ($\sim$ 100 ppm), Na, Ca, etc., just before pouring is also known to achieve modification of eutectic Si phase in Al–Si system. Similarly, P is known to modify the primary Si phase. The modification of Si takes place due to depression of eutectic point. Similar modification in size, shape and distribution of Si (additionally, Al dendrites in hypo-eutectic alloys) can be carried out by rapid solidification [49–53]. However, uniform modification of entire components (engine blocks) with widely varying cross-section is usually not possible.

In light of the above process and material limitations, laser surface engineering appeared to hold tremendous promise in treating engine cylinder bore surface for improved performance. Laser surface engineering was used to selectively melt and solidify the near-surface volume and thereby improve surface related properties particularly wear resistance. The high power density beam of laser causes melting in a confined region in the surface. Due to the conduction mode heat transfer through aluminum along with heat sink effect (self quenching) a high cooling rate (rapid solidification) is attained in small dimension (confined region). Hence, great refinement was achieved by laser surface engineering. There was substantial improvement in mechanical properties (measured from fracture study and nanoindentation), wear resistance, etc. [54,55]. Also, an interconnected network of eutectic phase mixture present in microstructure would reduce thermal conductivity.

A composite coating (>500 μm) or cladding was synthesized on A319Al using mineral iron oxides. Iron oxide of lowest oxygen to iron ratio (wustite) is a tribologically functional ceramic proven in plasma coating of cylinder bore [4]. Controlled/partial reductions of other mineral iron oxides have also been used. It is preferred to attain some degree of reaction-induced wetting of oxides. An Ellingham diagram suggests that Al readily reduces iron oxides to Fe known as metallothermic or aluminothermic reaction [56]. This is a highly exothermic reaction, often violent [57]. Age-old thermite welding technology uses this principle. Hence, the iron oxides are considered suitable candidate to attain reaction-induced wetting by liquid Al during LSE [57]. Since, LSE is associated with melting and resolidification of Al–Si alloy and reaction bonded or reacted iron oxide particulate reinforcement in Al matrix, the whole composite material is strongly bonded and adherent to the substrate (good particle-matrix bonding as well as coating-substrate bonding). The eutectic reaction in substrate, high cooling rate associated with LSE, and extreme thermal condition caused by violent thermite reaction can together produce a nanocomposite coating [58]. An exothermic reaction can provide a thick coating suitable for engine application. Nanoscale features improve hardness and strength also provides insulation owing to poor thermal conductivity.

6. Approach and progress

A319Al can be surface melted and rapidly solidified using a high power laser. The high cooling rate causes formation of very fine and uniform microstructure in the laser-modified layer. The cellular dendrite structure with soft aluminum cells and intercellular hard Si phases provide a microstructure conducive to formation of micro-channel and thereby more effective lubrications [59]. The entire coating thickness (~ 700 μm) was uniform both in microstructure and mechanical properties [54]. The refined and uniform microstructure and properties is due to high cooling rate and strong convective flow in laser melt-pool. The cooling rate and mixing can further be enhanced by exothermic reaction. The extra heat would result in higher thermal gradient and violent nature of the reaction would promote mixing. As discussed, iron oxide is being explored as a coating material.

In the present study, A319Al coupons were spray deposited with iron oxides or a mixture of iron oxides and aluminum (to ease initiation of reaction), followed by fusion by the laser beam traced in straight overlapping stripes over the entire surface of the samples. Fig. 3 shows the oxide particles fragmented during the laser treatment. Attaining temperature above 3000 °C is common in conventional thermite welding operations. Intense power input and conduction-mode heat transfer to substrate that acts as an infinite heat sink, in laser surface engineering often causes extremely rapid heating and cooling. Combined with highly exothermic thermite reaction, the solidification structures can alter extensively. The double exothermic reactions (reduction of iron oxides and reaction between Al and Fe to form aluminides) result in a violent process disintegrates the reactants and reaction products. Because of this thermal effect, the oxide particles are often fragmented to nanoscale. Fragmentation of dendrites was also observed resulting in nano particles.

Probing of the (laser) modified surface with features at nanoscale for various mechanical properties requires unconventional techniques. Instrumented Indentation Technique (IIT) or Nanoindentation has been regularly used to determine various mechanical properties of materials at nanoscale. The mechanical properties determined by IIT showed promise for engine application and are summarized in Table 1. IIT based evaluation of these coatings indicated that the extent of heterogeneity in mechanical properties was at nanoscale [54]. As seen from Fig. 4, a single indentation impression covers a large area comprising matrix as well as other particle reinforcements. There was no particular trend observed in properties while traversing from surface towards the substrate. This kind of effective homogenization across the coating thickness was achieved in rapidly solidified region owing to convective flow of liquid material and

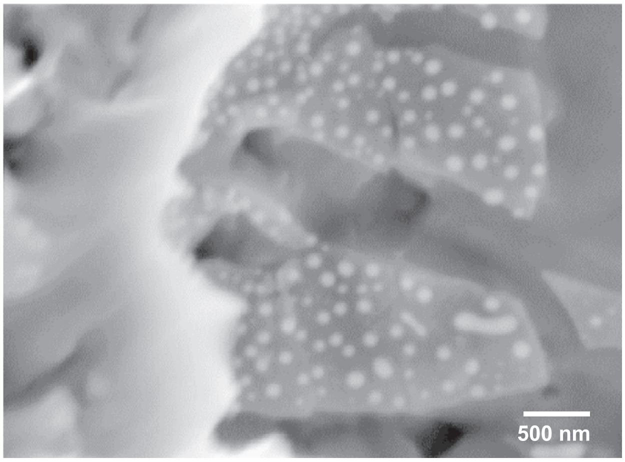

Fig. 3. Secondary electron micrograph of fragmented oxide particles.

Table 1
Nanoindentation (Berkovich and cube corner) data

Indenter	Depth (nm) or load (mN)	Hardness (GPa)	Elastic modulus (GPa)	Final displacement maximum displacement
Berkovich	200 nm	2.2	101	0.84
	500 nm	1.53	91.0	0.92
	1000 nm	1.30	86.6	0.914
	150 mN (~ 2200 nm)	1.25	75.5	0.9
Cube corner	400 mN	Not Calculated (calibration not valid for cube corner indenter)		0.98
	200 mN			0.98
	100 mN			0.98
	50 mN			0.98
	20 mN			0.98

violent reactions between oxide and matrix [60]. Besides mechanical properties such as hardness (*H*) and elastic modulus (*E*), the load displacement curves generated in IIT can provide information about mechanical deformation [61–64]. For example, the ratio between the final displacements to maximum displacement provides information about relative amount of plastic and elastic deformation. This ratio (between the final displacements to maximum displacement) for the laser induced rapidly solidified region was nearly 0.91, suggesting there would be little pile-up (Table 1) [65]. Although, iron oxide is brittle in nature, with even indentations of load up to 150 mN (about 2200 nm deep), the load–displacement responses did not show any signs of cracking with the Berkovich indenter. This may be due to high toughness associated with the composite (Al matrix with uniform distribution of fine iron oxide and other reaction product particles) nature of the rapidly solidified region. Fig. 4a shows scanning electron micrograph of typical Berkovich indentation impression, which confirms that there is no crack. Also, as suggested earlier, no pile-up was apparent.

Four-point bend test is a common method to determine strength of a coating. However, in case of coating on A319Al, the coating was too ductile. A cube corner indenter was thought to be suitable for fracture study since the threshold load for cracking is much less [66,67]. A set of indentation with five different loads (400, 200, 100, 50 and 20 mN) was carried out. Even for the largest load, the impressions indicate no sign of radial cracking. However, extensive pile-up was seen near the edges of triangular impressions (Fig. 4b). Examination of load–displacement curves for different loads also did not show any discontinuity in either loading or unloading curve, indicating there was no cracking. Hence, fracture mechanics approach to determine the toughness was not feasible in the present tough laser-induced rapidly solidified composite material. (Fig. 4a) [60]. Pile-up, without crack, indicates ability of the material to plastically deform. Table 2 summarizes the result of indentation done at different strain rates using Berkovich diamond. The results of this experiment are slightly different that Table 1 (1000 nm, 0.05 s^{-1}) because of the following: (1) this experiment was done in strain-rate control mode rather than displacement control mode; and (2) corrections due to thermal drift and possible creep were not applied. The indentation carried out at different strain rates confirmed that the indentation size effect was indeed a material effect.

A large number (~ 200) of indentations were carried out to determine the statistical behavior of the composite (Table 2). The properties corresponding to 200 nm inden-

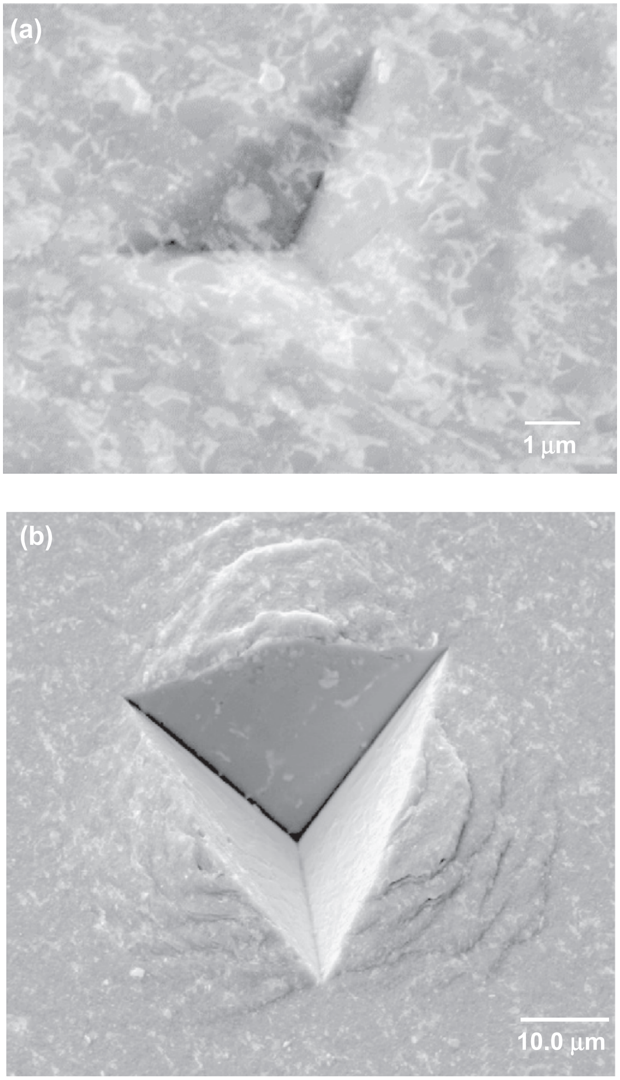

Fig. 4. Scanning electron micrograph of typical indentation impression with (a) Berkovich indenter and (b) cube corner indenter.

Table 2
Nanoindentation (Berkovich) at different strain rates

Strain rate	Hardness (GPa), standard deviation (%)		Elastic modulus (GPa), standard deviation (%)	
	Coating	Substrate	Coating	Substrate
0.005 (s^{-1})	1.54 (1.9)	0.89 (30)	82 (0.3)	75 (7)
0.05 (s^{-1})	1.44 (2.3)	1.03 (31)	82 (0.9)	79 (9)
0.5 (s^{-1})	1.42 (3.7)	1.1 (37)	77 (1.1)	53 (20)

tation depths were much higher along with a very large standard deviation [60,65]. As the depth of indentation increases, the standard deviation (for each measured parameters) gradually increases until about 400 nm, where there is a sudden increase in standard deviation even after accounting for tip rounding and indentation size effect; suggesting that it is essentially a material feature. It is well known that any microstructural features located as far as 10 times the depth of indentation affect the indentation behavior [68]. Close analysis of such behavior considering the stochastic probability of encountering the reinforcing phases suggested that the properties of this laser induced reaction composite coating varies in nanoscale order [65]. The IIT experiments now reveal that the mechanical properties are also in nanometer order suggesting a true nanocomposite.

Further investigation is currently on to evaluate this coating for engine application. The improvement reported in mechanical properties in conjunction with microscopic studies shows tremendous promise for engine application.

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