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FAILURE OF DIAMOND-LIKE CARBON (DLC) COATINGS IN AUTOMOBILE ENGINES – A REVIEW

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Abstract: *Diamond-like carbon (DLC) coatings have become very attractive for various industrial applications, such as cutting tools, automotive engines, biomedical implants, micro-electromechanical devices (MEMS). Due to their surface energies and ability to interact with lubricants to form surface protective films, good adhesion with substrate, increased wear resistance, improved electrical conductivity, decreased internal compressive stresses during deposition and thermal stability there are used in automobile components. In the automobile industry, DLC coatings are usually applied on combustion engine components such as piston, tappet, camshaft, piston rings and gudgeon pin, valve stem and head and rocker arm. DLC coatings helps in reducing friction and wear of the moving parts. However, there are challenges facing the use of DLC coated components during service, which are; internal compressive stresses, low adhesion and low thermal stability leading to failures such as rolling contact fatigue, micro-pitting, delamination, oxidation and scuffing. Hardness and internal compressive stress increase with increasing sp^3 content (sp^3/sp^2) ratio in DLCs. Internal compressive stress for DLC coatings $> 1\text{GPa}$ in tribological applications is not good, due to the elastic strain energy that drives fractures along the coating/substrate interface, leading to delamination through blistering. The addition of non-metals (Si, N, F or O) or metals (W, Cr, Ta, Ti, Mo or Cu) can improve thermal stability of DLC up to about $500\text{ }^\circ\text{C}$. Above, $500\text{ }^\circ\text{C}$ transformation of sp^3 to sp^2 begins to occur leading to graphitization. The addition of metals increases the interfacial fracture toughness and moderates the internal stress by creating two (2) interface; substrate/adhesion layer interface and adhesion layer/functional coating interface. This present paper will discuss the various failures that occur on DLC coatings such as internal compressive stresses, low adhesion and low thermal stability of non-metal and metal doped DLC coatings, regarding their applications in automobile engines. The effect of annealing conditions, tribological properties of non-metal and metal doped DLC, effect of sp^3/sp^2 ratio, and possible ways of reducing these failures on DLC coatings be discussed also.*

Keywords: *automobile industry, diamond-like carbon, energy consumption, internal compressive stresses, low adhesion, low thermal stability.*

1. INTRODUCTION

In the automotive industry the use of coatings which possess long-term stability having low friction coefficients and low wear rates at temperatures up to 500 °C are important for current developments, such as higher power densities, downsizing or the use of low-viscosity oils [1]. The use of diamond-like carbon (DLC) coatings are increasingly used in the automobile industry, mostly the hydrogenated amorphous carbon (a-C:H) coatings, even the hydrogen-free ta-C coatings are also gaining attention up to about 350 °C [2,3,4]. Incorporating additional elements can be used to modify DLC and increase the heat resistance of DLC coatings [5].

DLC coatings are commonly used for automotive engine parts (engine block, cylinder head, cylinders, crankshaft, connecting rods, pistons, sparks plug, fuel injectors, intake and exhaust valves, camshaft and belt) [6]. The main reason DLC coatings are used in automotive engine parts is simply due to the fact that it is a low friction coating, other reasons are; to circumvent the problems when using low viscosity oils, friction and wear resistance, constant change in oil additives and to reduce the use of anti-wear additives like Zinc dialkyldithiophosphates (ZDDP) [6]. It has been reported that DLC coatings reduces friction up to 30% in lubricated contact compared to steel/steel contact [7]. Energy lost to friction in a passenger car has been estimate as 33% [7].

2. ENGINE OPERATIONAL CONDITIONS

During the last 20 years, diminishing oil reserves and global warming has brought the awareness for the need to have a fuel-efficient and environmentally friendly transportation system. In this same period, automotive and lubrication engineers have intensified their efforts to reduce energy losses due to friction, rolling resistance, and cooling systems and to thereby boost the efficiency of the next-generation engines [8]. The main target of the automotive industry as they produce luxury

cars to attract customers is to cutdown on extra weight and fuel consumption [9]. High temperature is one of the causes of valve failure in internal combustion engine, which are also subjected to cyclic loading. Failure on the surface is as a result of elastic and plastic deformation, fatigue micro-crack and spalling [10]. These failures lead to increase in friction and wear on engine components, consequently causing high fuel consumption in engines of vehicles. Although, increase in the operational temperature of an automotive engine has some advantages, due to the fact that it directly influences the elements that bring about losses in the engine and effectiveness of the cooling system, and the formation of emissions gas in the engine. Increase in temperature raises the engine oil temperature and in turn lowers frictional losses in the engine, leading to an improved fuel efficiency [11].

Erdemir and Holmberg, 2015 [8] carried out a compressive study on energy consumption due to friction in motored vehicles. In automotive engines, rolling contact fatigue, micro-pitting, oxidation and scuffing are the tribology challenges encountered during operating conditions due to friction and wear [12]. The use of DLCs can overcome these challenges except for the issue of oxidation. This is due to the high temperature (150 to 180°C) involved, if exposed to high temperatures at operating conditions of the engine, they would be prone to oxidation [12].

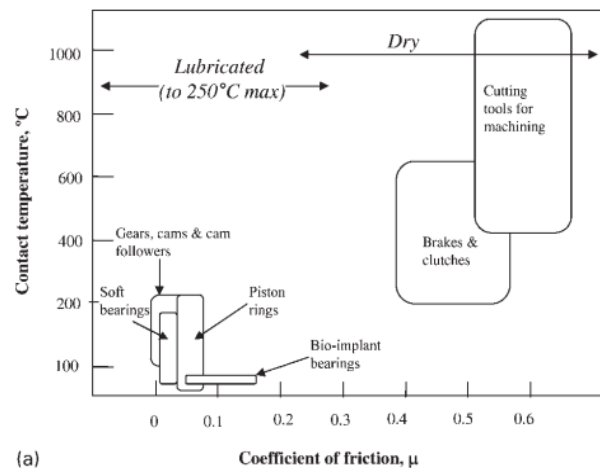


Figure 1. Friction–temperature regimes [12]

The temperature regimes for automobile lubricated engine components is 250°C (maximum) as seen in Figure 1. A decrease in friction coefficient and wear resistance of DLC films occurs with increase in temperature between 100 – 300 °C [13]. Piston ring coatings are required to resist a combination of surface degradation effects that encompass both chemical and mechanical processes. Since boundary lubrication occurs at the extreme displacement of the piston ring cylinder liner contact, the durability of the top piston ring requires resistance to wear [12].

2.1 Internal compressive stress and low adhesion

Internal compressive stress increases with increasing sp³ content (sp³/sp²) ratio. The effect of internal compressive stress is shown in Figure 2 for both hydrogenated and non-hydrogenated DLCs. High internal compressive stress value of 1 GPa are a potential achilles heel for DLCs in tribological applications which leads to the elastic strain energy that drives fractures along the coating/substrate interface and leads to coating delamination, sometimes via blistering [14]. Poor DLC coating adherence is an issue irrespective of the substrate. DLCs show variable adherence to Co–Cr–Mo, Ti–6Al–4V, cemented carbides, high speed steels, through hardened and stainless steels. To minimise this effect, coating architectures of the type shown in Figure 3 are invoked to locally moderate internal stress and increase interfacial fracture toughness. Here, at least one bond or adhesion layer is placed between the substrate and the multifunctional carbon coating. Accordingly, there are interface 1 (substrate/adhesion layer) and interface 2 (adhesion layer/functional coating). Either interface is a potential source for crack initiation and growth [12]. While, DLC coating adherence might be deemed satisfactory following scratch adhesion testing, such materials can nonetheless demonstrate poor adherence in various tribological applications. A further factor needs to be taken into account: the initiation and propagation of

fractures due to fatigue stress cycling [12]. This effect can be studied using high cycle surface elastic contact indentation testing of the kind reported by Ledrappier et al. (2008) [15].

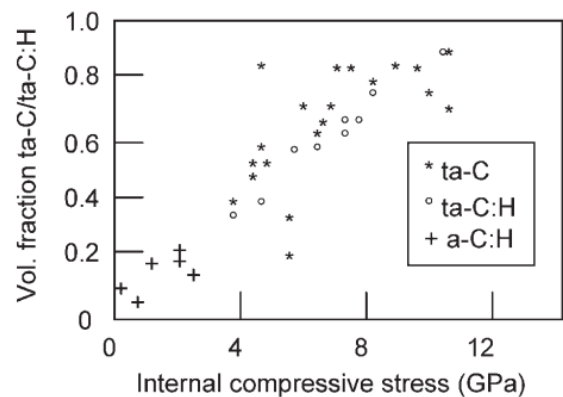


Figure 2. Variation of internal stress for ta-C and ta-C:H coatings as function of ta-C (sp³) content.

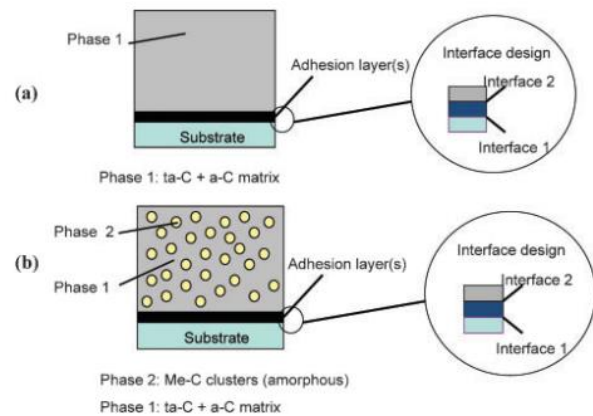


Figure 3. Typical non-hydrogenated DLC coating architectures (a) pure carbon multifunctional coating; (b) metal or non-metal doped carbon multifunctional coating [16]

2.2 Low thermal stability of non-metal and metal doped DLC coatings

It is very important to know the operating temperature range for an automobile engine in a passenger car in order to ensure that the provided coatings can withstand the effect of the maximum operating temperature. Studies have shown that several researchers have reported different operating temperatures; 85 to 155°C [17], maximum of 180°C [9], 250 to 300°C [18] and 750 °C to 950 °C [10]. Another author mentioned that the normal operating temperature conditions for an automotive engine is 80 – 100 °C, while some experimental studies have used as low as 22 °C

and as high as 500 °C [19]. Thermal stability (under vacuum) for hydrogen-free ta-C films deposited by CVAE are much more thermally stable than a-C:H films deposited by PACVD [20]. It was published in 1977 that the hardness of ta-C does not drop up to about 600 °C under vacuum [21].

It was observed that thin films in the thickness range of several tens of nm are stable up to at least 400 °C with only a very small graphitization under vacuum [22]. Investigations on very thin films (1.5 nm) showed that changes observed in the Raman peak position and ID/IG of the 300 °C annealed samples (time 60 min) are not attributable to graphitization. The ta-C film at 300 °C showed only more sp² clustering and not a reduction in sp³ content [23]. Oxidation for diamond films in air started at about 640 °C [24]. Different graphite grades have been investigated and results showed that almost no oxidation at 330 °C for 1 h, while at 530 °C had a significant oxidation rate depending on the graphite grade [25]. The starting temperature of oxidation for a-C and ta-C films varied depending on structure. It has been shown that for a-C and ta-C films deposited by FCVAE, the oxidation behavior depends strongly on the sp³ content [26].

3. FAILURE OF DLC COATED AUTOMOBILE COMPONENTS.

Failure modes for 100Cr6 rollers are summarised in the schematic diagram (Figure 4). Failure of the uncoated 100Cr6 rollers is usually due to the occurrence of large, rolling contact fatigue (RCF) pits, which resembled those classified as type IIIA [12]. In addition, smooth wear also prevail, which is evident from the polishing away of the original surface grinding marks. RCF pitting was typically observed after several hundred hours of testing and also affected some of the coated rollers being classified as types IIIA and IIIB failures, although the size (surface areas) of these particular rolling contact fatigue failures were approximately 30–50% smaller than those observed for the uncoated rollers [12]. In some cases, RCF pitting was initiated after shorter

times than those observed for the uncoated materials. An unexpected mode of failure was that due to micropitting (mode type IV). This mechanism prevailed to a varying extent on all the coatings tested, but did not cause complete coating failure. Coating delamination is a serious problem, there are three kinds of failure modes, types IA, IB and IIB (Figure 4) [12,27]. On the W-doped DLC (Cr–W–C:H), type IA and IIB caused delamination of the nanolayers that comprised the architecture of this coating. The type IA or IB failure modes took place for the Cr₂N and CrNzC coatings, either along interface 1 or interface 2 (as seen in Figure 3) [12]. None of these delamination failure modes affected the more uniformly structured W-doped DLC (W–C:H). Here, eventual failure is rate controlled through microabrasion and a feature of this wear is the formation of banding patterns shown in Figure 5.

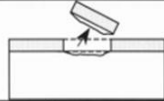
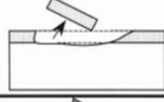




Failure Mode	Representation	Characteristics
Type IA		Delamination of the coating along and/or slightly beneath the coating-substrate interface. No polishing (smooth) wear of coating.
Type IB		Mild polishing (smooth) wear of the coating and subsequent delamination along and/or slightly beneath the coating-substrate interface.
Type II		Micro/nano-delamination of the coating outer layer(s) in combination with polishing (smooth) wear.
Type IIIA		Macro-pitting (rolling contact fatigue) and coating delamination.
Type IIIB		Severe polishing (smooth) wear of the coating and subsequent rolling contact fatigue of the substrate. Also affects uncoated rollers.
Type IV		Micro-pitting of the coating (pits <10µm)

Figure 4. Principal failure modes of hard coated bearing surfaces observed during high pressure lubricated contacts [27]

Two types of carbon coating, one based on non-hydrogenated a-C and the other based on ta-C, were applied to 100Cr6 substrates and subjected to the same rolling/sliding contact described earlier. Here, a simple base oil containing no specific additive package was used. For both kinds of carbon coated 100Cr6, type IA coating delamination took place after a relatively few test cycles (Figure 6) [12].

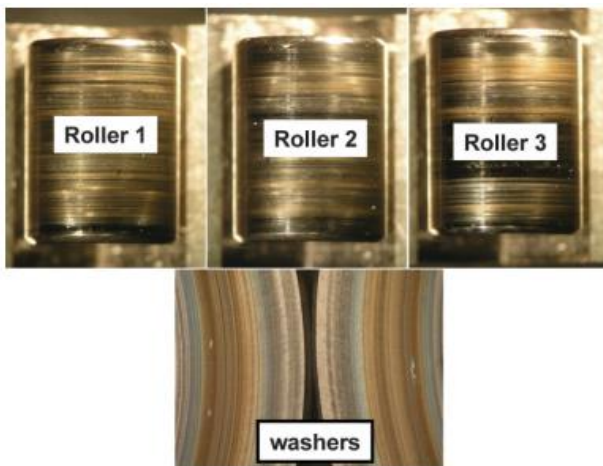


Figure 5. Microabrasion of W doped DLC (W-C:H: type B) coating on 100Cr6 test bearing rolls and corresponding uncoated washers.

The effect was studied more carefully and it was demonstrated that the delamination phenomenon, although exhibiting wide scatter, followed an S-N behaviour that is typical of fatigue (Figure 7).



Figure 6. Delamination failure of ta-C DLC coating on 100Cr6.

This suggests that crack propagation along interfaces 1 or 2 (Fig. 3) occurs at a rate that depends upon the magnitude of the change in stress per unit cycle and the total number of stress cycle reversals, this means crack growth is due to a fatigue mechanism.

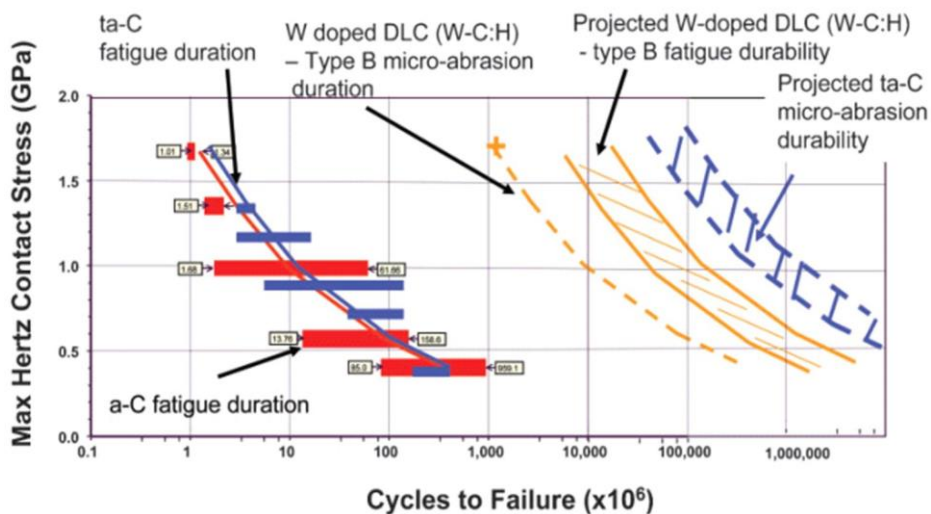


Figure 7. Coating life for indicated carbon coatings on 100Cr6 and their failure mechanisms.

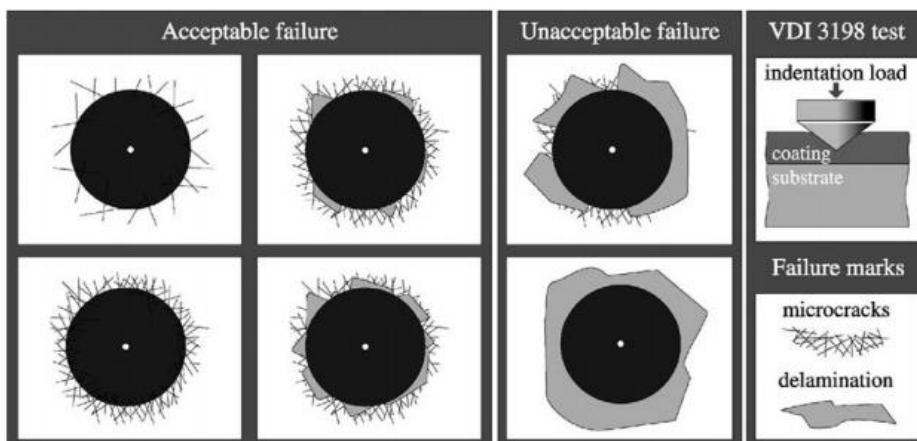


Figure 8. The principle of the VDI 3198 indentation test.

Accordingly, fatigue delamination and microabrasion processes are competing failure modes for carbon based coatings in this application. For the non-hydrogenated a-C and ta-C enriched carbon coatings, failure was dominated by delamination in Figure 7, while the hydrogenated W-doped DLC type B failures, contained lower internal stress (approximately 800 MPa), compared to (approximately 3 GPa) for the ta-C coatings failed progressively by a process of microabrasion (Figure 5). If delamination fatigue failures could be mitigated for non-hydrogenated a-C and ta-C enriched carbon coatings by significantly reducing internal stress, then more durable coated 100Cr6 with projected life cycles moving towards the right hand side in Figure 7 [12].

The result of adhesion quality of the DLC film on Inconel Alloy 718 samples resulted to be very good according to the VDI 3198 standard (see Fig. 8), which are classified into acceptable and unacceptable failure for delamination fault. Some very small radial cracking of the film can be observed on the samples around the indentation region [28].

4. IMPROVEMENT OF DLC COATINGS FOR AUTOMOBILE APPLICATION.

Different modified DLC coatings have been investigated with regard to their mechanical and tribological properties up to 550 °C. The results of these investigations form a basis for being able to define friction- and wear-reducing DLC coatings for automotive components for use at higher temperatures (Figure 9a & 9b) [5].

4.1 Effect of annealing on the thermal stability of DLC coatings.

DLC coatings are usually associated with internal stresses, which affects the tribological properties and thermal stability of the coatings. Annealing is always used to reduce the internal stress in DLC coatings. Annealing ta-C up to 800 °C reduces the internal stress to an insignificant value (Figure 10) [21,26]. However, annealing DLCs above 500 °C

reduces the thermal stability. Figure 11, shows two carbon films deposited with different bias voltages, the lower hardness film having a lower sp³ fraction. Two (2) decades later it was revealed that the mechanical properties, hardness and elastic modulus remain almost stable with annealing up to 850 °C for ta-C coatings with sp³ content of 85% [21,26].

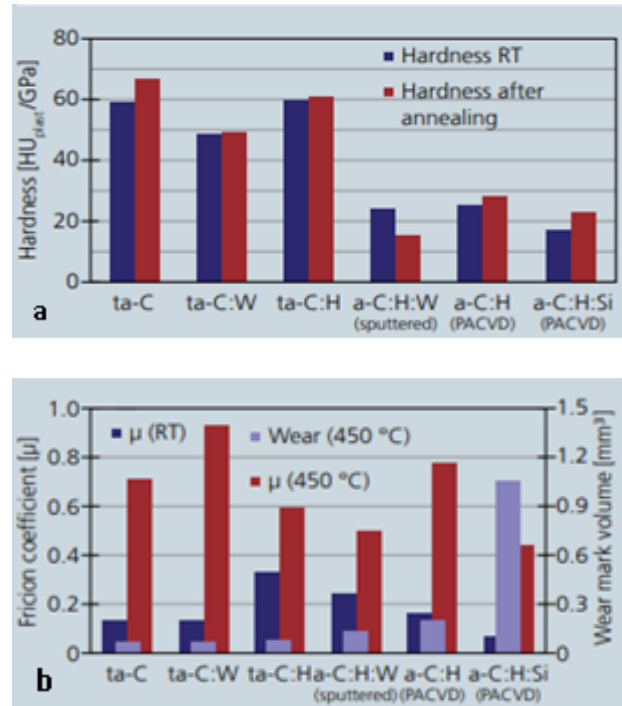


Figure 9. (a) Hardness before and after annealing, (b) Friction coefficients and wear rates after the at room temperature and at 450°C

During the annealing process a clustering of the sp² bonded carbon atoms occurs first [30,31], and the sp³ content is not affected. That process results in the change of some physical properties, and a reduction in compressive stress [30].

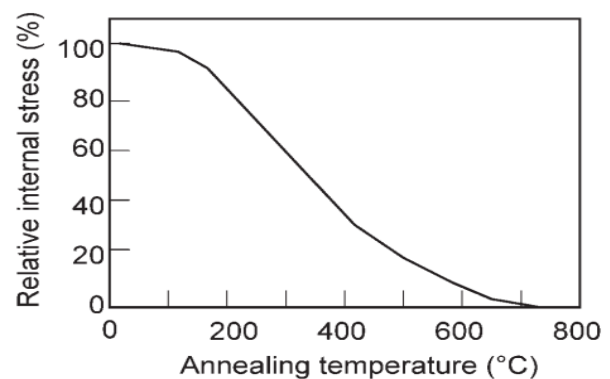


Figure 10. Relative internal stress (%) against annealing temperature (°C) for ta-C coatings deposited at room temperature [12]

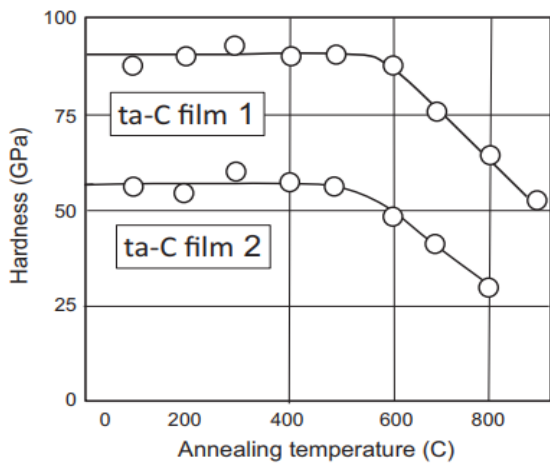


Figure 11. Micro hardness versus annealing temperature for ta-C films deposited using DCVAE with different bias voltages [21]

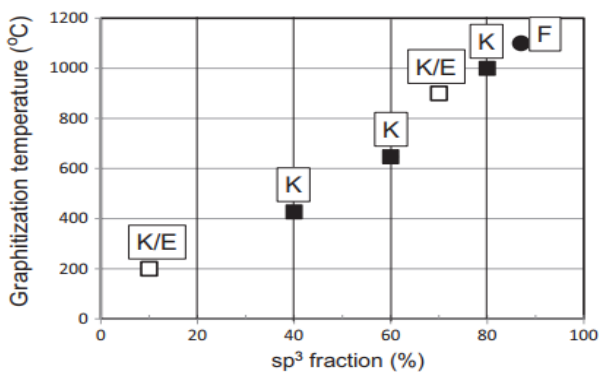


Figure 12. Graphitization temperature for a-C films versus the sp3 fraction [30,31]

At higher temperatures graphitization begins, Figure 12, shows the graphitization temperature for a-C films having different sp3 fractions, deposited by argon ion beam sputtering (IBS), mass-selected carbon ion beam (MSIB) deposition, pulsed-laser deposition (PLD), and filtered arc (FCVAE) deposition [23]. In Figure 12, points K/E are estimated values for low sp3 (IBS) and high sp3 (PLD) films, points K is measured values for MSIB film and point F is an FCVAE film [30,31]. The best thermal stability, up to approximately 1100 °C, was shown by the film with the highest sp3 fraction, deposited by FCVAE. By 1200 °C the sp3 fraction of this coating was decreased to 20% [30]. The confirmation of a strong correlation exists between the sp3 fraction and the graphitic transformation temperature by the investigations of the evolution of bonding structures of a-C films and the electrical resistivity during laser annealing [32]. Figure 13 shows the plot of loss

in film thickness against annealing temperature for films (initial thickness of 450 nm). It can be observed that films with higher sp3 fraction retain their structure up to 500 °C, and a lower rate of material loss during heat treatment. The oxidation rate (thickness loss) becomes significant only above 500 °C for the ta-C film, whereas the a-C films with the low sp3 content begins to lose thickness above 450 °C and almost completely at 475 °C. The friction torque of the valve train for various surfaces as a function of the rotation speed (Figure 14). Using ta-C coating gave a reduction of 45% in the friction torque at 2000 rpm compared to the standard phosphated surface treatment [23].

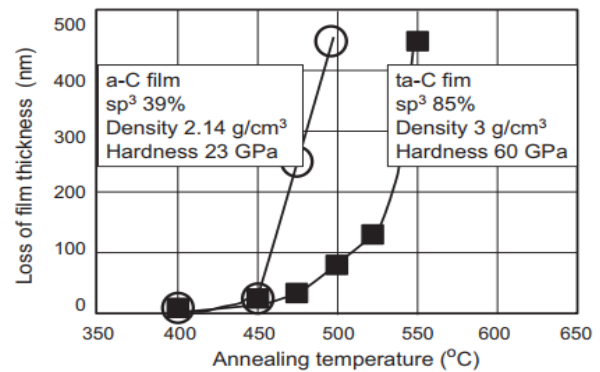


Figure 13. Shows loss in film thickness as a function of annealing temperature in air for 2 h, for a-C and ta-C film deposited by FCVAE [26]

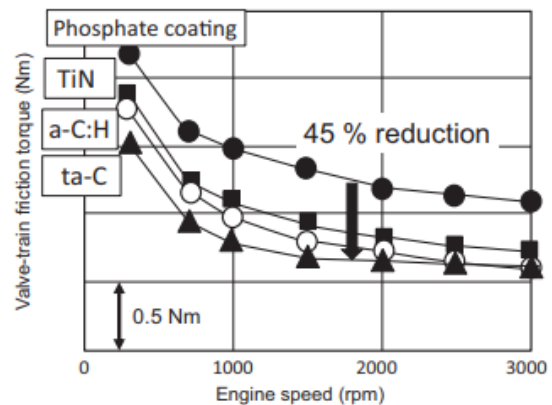


Figure 14. Friction torque of the valve train for various surfaces as a function of the rotation speed [23]

4.2 Non-Metal and metal doping of DLC coatings

Metal-doped DLC (Me-DLC) coatings usually exhibit higher thermal stability than

non-doped DLC up to annealing temperatures of 500°C, which was revealed by X-ray diffraction, transmission electron microscopy, and Raman spectroscopy.

Annealing temperature above 500°C, losing high amount of hydrogen from the Me-DLC coatings, causing breakdown and structural collapse of the coatings at high temperature, which may be due to breaking of C-H bonds. Thereby, the C-C networks become graphite-like, leading to the formation of volatile C-O and metal oxides phases [33]. Since 1971, DLC has been widely used in automotive industry, this is simply due to their excellent tribological properties such as low friction, wear and corrosion resistance, high hardness, high thermal and chemical stability. Non-doped hydrogenated DLC coating has low resistance to wear in lubricating oils containing MoDTC, this is due to the decomposition and chemical reactions that formed oxides and nanocrystallites [34]. Si-doped DLC coating produces anti-wear film which is stronger in the presence of additives in lubricants but weaker in the absence of additives. Raman spectroscopy is used to characterize the tribo-chemical process for the DLC coatings in the presence of additives in lubricants. PVD process was used to deposit tungsten-doped diamond-like carbon (a-C:H/W) on AISI 52100 bearing steel [34].

It has been observed that addition of Mo delays graphitization up to 400°C in air and at 500°C in low pressure atmospheres, the addition of Mo₂S leads to an increase in the thermal stability by a decrease in the graphitization rate. Molybdenum oxides act as abrasive particles providing hardness and stability at high temperatures, simultaneously damaging the formed tribolayer which promotes lubrication. MoO₃ above 500°C become volatile so at high temperatures the coefficient of friction will change due to formation of a new tribolayer, which helps to decrease the friction. Mo-DLC coatings tends to form a granular pattern (onion-like) structure whose density is reduced as the carbon content increases in the matrix, while reducing hardness. An industrial sized Hauzer HTC 1000-4 PVD coating machine which

combines UBM (Unbalanced magnetron) and HIPIMS (High power impulse magnetron sputtering) was used for the deposition [35]. Mo-doped diamond-like carbon coatings were deposited by closed field unbalanced magnetron sputtering to determine their mechanical and blood compatibility properties. The undoped and Mo-doped DLC coatings were analysed by Raman spectra, Atomic force microscopy, and temperature-dependent frictional wear testing. The obtained results indicated that the Mo-DLC coatings with low Mo concentration was a more efficient protective coating with reduced residual stress, increased cohesive strength and good wear resistance at temperature of 500°C [33].

5. CONCLUSION

In conclusion, the need of DLC coatings for automobile engine components were discussed, engine operational conditions, internal compressive stress and low adhesion, low thermal stability of non-metal and metal doped DLC coatings, failure of DLC coated automobile components, Improvement of DLC coatings for automobile application, effect of annealing on the thermal stability of DLC coatings, non-metal and metal doping of DLC coatings were also discussed. The challenges faced with the use of DLC coated components during service, which are; internal compressive stress, low adhesion and low thermal stability, which leads to failure of engine components such as rolling contact fatigue, micro-pitting, delamination, oxidation and scuffing. Internal compressive stress can be reduced by annealing, adhesion can be improved by the use of substrate/adhesion layer and adhesion layer/ coating interface, while low thermal stability can be overcome by non-metal and metal doping of DLC. These solutions reduce the failure of DLC coatings and make them suitable for coating automobile engine components.

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