

Sung Chul Cha · Ali Erdemir *Editors*

Coating Technology for Vehicle Applications

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Preface

In recent years, many books, journal articles, and conference proceedings have been published to address both theoretical and experimental aspects of various surface engineering and coating technologies, but a complete and comprehensive book that is solely devoted to the arts and sciences of coatings that are intended for vehicle applications has been missing. For the present book, we contacted many well-known and qualified experts from universities, research institutes, and coating and automotive companies and asked them to contribute chapters that focus on the practical and industrial-scale vehicle applications where low friction, high wear resistant, and improved reliability for powertrain, body, chassis, and interior and exterior parts are needed. The principal audience for this book includes the broader scientific, academic, and industrial communities interested in automotive and related topics or products.

Over the last several decades, the realization of a sustainable transportation future that is also environmentally viable has become one of the major goals of many industrialized nations. In the transportation sector, there are also constant demands for increased safety, lower cost, and new features, as well as long-term reliability and reduced cost-to-performance ratios over the useful life of the vehicle. In addition, customers have been putting more value on such factors as aesthetic design, high comfort and luxury, more robust driving experience, and uniqueness. Furthermore, the increasing demand for higher energy efficiency and environmental compatibility of passenger cars and other vehicles has necessitated the use of more advanced friction control technologies in many moving mechanical components. The current emission level for carbon dioxide is expected to decrease by approximately 27 % in 2020 due to improvements in fuel economy. Achieving this goal requires friction reduction of moving automotive parts through improved coating technology and their resultant increase of fuel efficiency, in addition to incorporation of advanced high strength steels, powertrain downsizing, and selective use of lightweight materials. The topics to be covered in this book will highlight how energy efficiency can be improved in engines by the use of advanced functional coatings. Reduced fuel consumption will ultimately result in lower emissions and, hence, fewer environmental problems.

As stated above, this book focuses more on practical applications of coatings on various automotive parts than on their theoretical and fundamental aspects, which have been well covered in earlier books and journal articles. Obviously, coating technologies have evolved over a long period of time, but their uses in various vehicle applications in large volumes did not really start until the early 2000s. Some of the major roadblocks were high production costs and difficulties in the mass production on a repeatable/reliable manner. With the advent of physical and chemical vapor deposition technologies and other breakthrough developments in mass production, the cost came down, and the quality—and hence the wear lives—of coatings has improved tremendously. Among others, the development and large-scale implementation of diamond-like carbon films (DLC) for vehicle applications have made a great positive impact in the automotive and other industrial fields. These coatings are now used in huge quantities and applied on many moving mechanical parts of an engine. Historically, the inception of DLC goes back to the mid-1950s, but it took more than two decades until work on them by Aisenberg and Chabot in the 1970s, as well as Koidl in the 1980s, together sparked greater interest in this coating. These and other efforts throughout the 1990s culminated in the large-scale application of DLCs in various engine parts to achieve low friction and high wear resistance. The competition for enhanced fuel efficiency and vehicle performance among many car makers was perhaps one of the key reasons for the strong entry of such parts into the automotive field. With increased awareness over the connection between CO₂ emissions and climate change and subsequent tighter environmental regulations, car makers have increasingly paid attention to technologies that can save fuel and, hence, reduce emissions. In general, all these factors have had a positive effect on attaining accelerated development and application of advanced coatings in the automotive industry.

This book is intended to fill an important void and provide key information on the state-of-the-art coating technologies used for vehicle applications. The major thrusts include (1) low-friction and wear-resistant coatings in powertrains, (2) recent advances in scale-up and cost reduction of coating technologies for large-scale automotive applications, (3) coatings for metal-forming dies that can be used for advanced (or ultra) high strength steel sheets, (4) coatings for increasing safety and reliability, (5) advances in surface technologies, e.g., texturing and patterning, (6) coatings that provide increased functionality and decorative appearance of automotive parts, and (7) thermal spraying applications.

Recently, many commendable efforts have been directed to research and development on novel coating materials, surface, structure, and interface design, lower temperature and higher rate deposition, more effective bonding, and roughness control. There is no doubt that more efforts will be spent in the coming years to expand the uses of coating technologies for vehicle applications, and all of these efforts will make future vehicles much safer, more durable, highly efficient, and eco-friendlier. In particular, combinatorial uses or applications of more than one type of surface engineering or coating technology will create a truly multifunctional surface that can meet the needs of future vehicles. The ultimate goal of this book is to provide valuable information for future researchers and engineers on the vehicular uses of

advanced coating technologies and thus motivate continued research and development that can help in the realization of a sustainable transportation future.

The editors thank the authors of each chapter and also acknowledge the support of their respective institutions: Hyundai Motors Company, Korea, and Argonne National Laboratory, USA. Lastly, they thank their families and friends for their help and understanding during the preparation of this book.

Seoul, Korea
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Editors' Biography

Sung Chul Cha is a Senior Research Engineer at the Hyundai Motor Group, Automotive, Research and Development Division, in Hwaseong, Korea. He received his Diploma of Engineering (1998) and a Doctor of Engineering degree (2001) in Georesources and Materials Engineering from RWTH Aachen, Germany. In 2002 he became a research associate and postdoc at the Department of Interface Chemistry and Surface Engineering at the Max Planck Institute for Iron Research (MPIE), Düsseldorf, Germany, and continued his research in the field of high temperature materials and reactions including coating technology. In 2005 he began work in the area of materials engineering and material properties at Siemens Power Generation, Mülheim a.d. Ruhr, Germany. Since 2007 he has been employed at the Hyundai Motor Group and responsible for the development of automotive materials.

Dr. Cha has published over 20 scientific papers and holds more than 30 international patents.

He was a keynote speaker, chair, and reviewer of the session on “Coated Materials” (2014) and a reviewer and chair of the session “Automotive Tribology” (2013) at the SAE World Congress & Exhibition and he was an invited keynote speaker for the SVC 2014 Conference.

Ali Erdemir is an Argonne Distinguished Fellow and Senior Scientist with international recognition and significant accomplishments in the fields of materials science, surface engineering, and tribology. He received his B.S. degree from Istanbul Technical University in 1977 and M.S. and Ph.D. degrees in Materials Science and Engineering from the Georgia Institute of Technology in 1982 and 1986, respectively. His discoveries of nearly frictionless carbon and superhard nanocomposite coatings, as well as a range of novel nanolubricants and lubrication additives, have been hailed as major breakthroughs in the field.

Erdemir's research is directed toward nanoscale design and large-scale manufacturing of new materials, coatings, and green lubricants for a broad range of applications in manufacturing, transportation, and other energy conversion and utilization

systems where further increases in efficiency, reliability, and environmental compatibility are the primary objectives.

Erdemir has received numerous awards, including five R&D 100 Awards; holds 16 U.S. patents; and has published more than 290 papers, 18 invited book and hand-book chapters, and two edited books. He is a Fellow of ASME, STLE, AVS, and ASM-International.

Chapter 1

Energy Consumption Due to Friction in Motored Vehicles and Low-Friction Coatings to Reduce It

Ali Erdemir and Kenneth Holmberg

Abstract During the past two decades, global awareness and societal needs for more fuel-efficient and environmentally friendly transportation systems have increased considerably because of the diminishing oil reserves, skyrocketing fuel prices, and much tougher governmental regulations to combat greenhouse gas emissions. During the same period, automotive and lubrication engineers have intensified their efforts to reduce parasitic energy losses due to friction, rolling resistance, aerodynamics, and cooling systems and to thereby boost the efficiency of next-generation transportation vehicles. In comprehensive studies involving light, medium, and heavy-duty vehicles (Holmberg et al., Tribol Int 47:221–234, 2012; Holmberg et al., Tribol Int 78:94–114, 2014), it was determined that nearly one-third of the fuel energy is consumed to overcome friction generated by engines, transmissions, tires, and brakes. Among these, energy losses due to friction in engines and transmissions were reported to be among the highest. The same studies have also advocated that with the adaptation of advanced friction control technologies, energy losses due to friction could be reduced markedly, and such improvements in energy efficiency can, in turn, translate into significant reductions in greenhouse gas emissions. The main purpose of this chapter is to provide an overview of the impact of friction on energy consumption in vehicles on a global scale and of the recently developed and emerging friction control technologies that can further improve the fuel efficiency and eco-friendliness of future transportation vehicles.

Keywords Energy efficiency • Emissions • Friction • Internal combustion engines • Low-friction coatings

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1.1 Introduction

Friction has always been and still is a fascinating physical phenomenon. Throughout history, it has captured the curiosity of humankind because of its many effects on our way of life. In particular, humankind has always searched for new means to reduce the adverse impacts of friction for smooth and safe mobility. Prime examples are the transportation of huge colossus and stones on lubricated pathways by many slaves to their designated locations along the river Nile in ancient Egypt and the use of animal fats by early Egyptians and Mesopotamians to lubricate the wheel hubs of chariots [1, 2]. The lubrication of wheels and other moving parts in transportation vehicles has not essentially changed since then, but the type of lubricants used nowadays has gotten far more sophisticated and, hence, more effective. Overall, in this modern era of high mobility and global industrial activity, lubricants have become an integral part of our daily life, and without them, high friction and wear would prevail and waste energy, reduce machine life, and cause harmful emissions.

Since the beginning of the industrial revolution, many scientists and engineers have been exploring the root causes of friction and wear and means by which they can be controlled to reduce their adverse impacts on energy, the environment, and component durability. As a result of these steadfast efforts, myriad scientific insights have been gained on the mechanisms behind friction and wear, and novel solid and liquid lubricants have been developed to alleviate their deleterious effects on all kinds of moving mechanical systems. Figure 1.1 is an illustration of how friction has been reduced over the past few decades alone by the development and implementation of various materials and lubrication technologies. Certainly, reduced friction translates directly into higher efficiency in all mechanical systems, while less wear ensures reliability and longer life as well as lower maintenance costs.

To reduce the adverse energy and environmental impacts of fuel consumption, increasingly tougher fuel economy and emission standards have been instated by

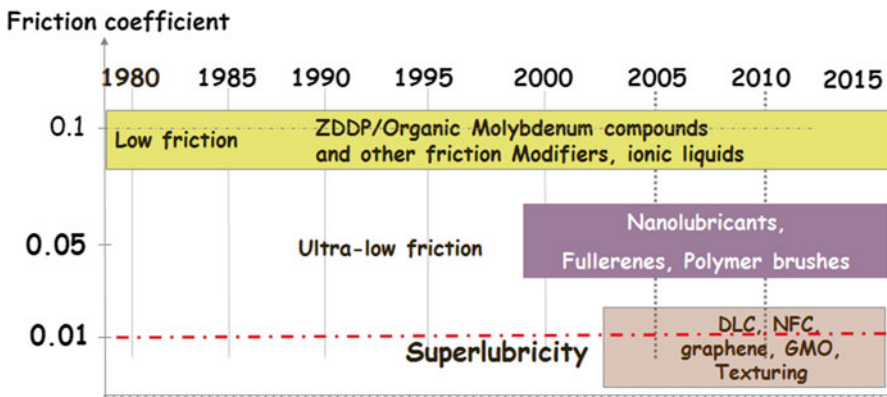


Fig. 1.1 Progress in friction control technologies over the years (adopted and updated from J.-M. Martin)

many industrialized and developing nations in recent years. For example, the US government has steadily increased the Corporate Average Fuel Economy (CAFE) standard over the years, and for new passenger cars in 2025, the target is 54.5 miles/gallon. In addition, the Environmental Protection Agency (EPA) has reduced its fleet CO₂ emission target to about 160 g per mile by 2025. If we consider the fact that in the USA alone, the transportation sector consumes about 14 million barrels of crude oil per day and is also responsible for about 32 % of the CO₂ emissions; the urgency of improving efficiency and reducing emissions in vehicles becomes very clear.

Increasingly tougher efficiency and emission standards mentioned above are driving transportation and related sectors (like engine materials, lubricants, and additives) to develop and implement newer and better materials and lubrication technologies that can help meet the efficiency and emission targets, with an ultimate goal of achieving a truly sustainable transportation future. These higher performance materials and lubricants are also essential for achieving higher power density by engine downsizing and for meeting the more stringent operating conditions of advanced turbochargers, new valve train designs, and direct injection technology. Accordingly, much increased activities have been devoted to both the materials and lubrication areas to further reduce friction- and wear-related energy losses in engines and other moving mechanical systems.

On the materials' side, several tribological coatings, like diamond-like carbon (DLC), have been developed and used in engines to reduce friction [3–5]. Certain DLC films were shown to provide friction coefficients of less than 0.01 under the boundary-lubricated sliding regimes when used in combination with specially formulated engine oils. However, progress in bringing these super-low-friction technologies into full-scale industrial practice has been rather slow. Most of the novel lubricants affording superlubric sliding regimes are either very expensive or restrictive in their uses, i.e., they only work under operational or environmental conditions that are not typical of modern engines, where typical operation spans over broad ranges of loads, speeds, temperatures, and environmental conditions [6]. Some of the low-friction materials and lubricants mentioned are also challenging to apply or incorporate into conventional engine components or other mechanical systems. What is really desired in most practical applications is that the new and more advanced lubricants have little or no restrictions on their uses, are compatible with existing lubrication technologies, are environmentally benign, are long lasting, and are affordable and easy to implement.

As is clear from the foregoing, more work is needed to reduce the intensity and adverse effects of friction on efficiency, durability, and environmental compatibility of all moving mechanical systems, including motored vehicles. Moreover, if we consider the lifecycle analyses for materials and services used in the making of a vehicle as well as the well-to-wheel type energy losses incurred during the production of fuels and lubricants, the actual amounts of energy spent would undoubtedly be much higher. Besides, it is important to remember that frequent remanufacturing and/or replacement of worn parts due to friction- and wear-related failures also consume large amounts of energy. Along the same lines, one has to consider the energy spent to recycle a used up or failed vehicle at the end of its lifecycle.

According to the latest statistics, the number of motored vehicles on our planet is more than 1 billion, and this number is projected to grow even further in the near future, mainly because of the rapid expansion of transportation markets in developing countries like China and India [7]. Unfortunately, the fuels powering these vehicles still mostly come from nonrenewable energy sources like petroleum. When they are burnt in the combustion chambers of engines to generate power, large amounts of CO₂ and other gaseous emissions are created and released to the environment. Globally, the transportation sector accounts for a significant portion of the CO₂ emissions, as will be elaborated in the following sections.

1.1.1 Impact of Friction on Fuel Economy and CO₂ Emission of Motored Vehicles

As is clear from the foregoing, friction and wear between moving mechanical components of an engine affect its fuel economy, emission characteristics, and lifetime. Accordingly, the key focus of recent lubrication and engine R&D has been on reducing friction and wear and, hence, lowering fuel consumption and emissions [8]. A recent comprehensive study by Holmberg et al. [9] estimated that nearly one-third of the total fuel (amounting to 2×10^{11} l) used by cars is spent to overcome friction and other mechanical and hydrodynamic losses in engines, transmissions, tires, and brakes. This means that globally, one passenger car uses about 340 l of fuel on the average per year to overcome friction for an average driving distance of 13,000 km/year [9]. Overall, 360 million tons of oil equivalent per year (Mtoe/a) or 7.3 million TJ/a is lost to friction. Energy losses due to friction in the engines and transmission systems were found to be among the highest and estimated to account for about 28 % of the total fuel energy consumed.

Fuel burnt to power transportation vehicles turns primarily into H₂O and CO₂, which are then released to the environment through the tailpipes of vehicles in huge volumes every day. The gradual accumulation of CO₂ in the upper atmosphere is suspected to cause climate change. According to well-established statistics, back in 2009, the overall transportation share of the world's CO₂ emission was around 18 %, as will be discussed later. The same sector consumed about 20 % of the world's total energy output during the same year. Among all transportation vehicles, ground or road transportation consumed most (i.e., more than 70 %) of the energy and accounted for 80 % of the total CO₂ emissions. Therefore, any progress in further reducing friction in transportation vehicles would be most welcome news for the realization of a sustainable transportation future that is also environmentally responsible. When we consider other industrial operations, like manufacturing, power generation, mining, steel industry, paper and pulp, and forest industry, the enormous importance of friction in energy security and environmental sustainability becomes very clear [10]. Other gaseous pollutants besides CO₂ (e.g., NO_x and SO_x), which are also generated during combustion, are well known for their adverse impacts on our ecosystem, in general and public health in particular (as they are blamed for millions of acute lower and upper respiratory symptoms each year).

1.1.2 Impact of Lubricants on Fuel Efficiency and Emissions

As well appreciated by many lubrication and automotive engineers, for smooth, safe, and long-lasting operation of all moving mechanical parts in an engine, the use of an advanced lubricant is a must. Besides reducing friction and wear, these lubricants provide many other important functions, such as preventing oxidation and corrosion, eliminating varnish and deposit formation, and increasing resistance to thermal degradations and other environmental effects (water buildup, seal compatibility, etc.), as well as minimizing the adverse impacts of combustion products such as soot, ash, and other particulate matters [11, 12]. Such lubricants can also mitigate frequent remanufacturing and/or replacement of worn parts due to mechanical friction and wear, which consume large amounts of energy. Because oils' performance degrades in the long run and poor or inefficient lubrication results in higher friction and hence larger energy losses in a motored vehicle, timely oil change is thus a good practice for reducing maintenance cost and sustaining good fuel efficiency [13].

It is important to remember that lower fuel consumption means lower volumes of CO₂ and other types of pollutions are being generated and released to the environment. Therefore, in recent years, efforts to develop new lubricants that can lead to even much higher fuel economy and lower emissions have gained significant momentum. Undoubtedly, besides effective lubricants, such improvements can also be attained by the development of lighter vehicles that can also run on electricity. However, in most transportation vehicles, including the lighter and electric-powered ones, the development and uses of advanced lubricants and additives are still essential for overall improvements in vehicle life, performance, efficiency, and emissions [13–15].

Accordingly, lubricant companies have been working on newer synthetics that can afford higher resistance to heat-related degradations yet still maintain desirable levels of viscosity and other physical characteristics, despite increasingly harsher engine operating conditions [16, 17]. Interest in polyalkylene glycol and other types of synthetic oils providing much lower viscosities has also increased recently and already resulted in some industrial applications. In addition, bio-derived or blended lubricants (such as bio-olefins) are making their ways into the marketplace as the supplies of petroleum-based products may dry up in the distant future, and synthetic products may not be able to close the gap. Additive companies have been working very hard toward the development of more environmentally benign antifriction and antiwear additives (ionic liquids, nanoparticulate additives, ashless organic friction modifiers, etc.) to potentially replace or complement the performance of traditional additives, such as zinc dialkyldithiophosphate (ZDDP) and molybdenum dithiocarbamate (MoDTC), which add up to ash content and poison aftertreatment catalysts in engines [15, 18].

1.1.3 Novel Combustion Regimes and Weight Reduction Strategies

To improve the fuel economy of future vehicles, manufacturers have been redesigning their engines to attain better combustion regimes (use of homogeneous charge compression ignition, smaller displacement engines, cooler combustions,

laser ignition, etc.) that can potentially improve the overall combustion process and, hence, produce less pollution while delivering more power and higher fuel economy. For a long time, weight reduction has been a key strategy of most manufacturers in the transportation sector for improving fuel economy of cars and trucks. As a result, significant progress has been made on this front, and substantial fuel savings have already been achieved by using lighter materials (such as Al and Mg alloys) in structural body parts, engine blocks, and other components [19]. Overall, with the adaptation of even lighter materials (such as carbon fiber-reinforced polymeric materials) and more advanced friction control technologies (super-low-friction materials and coatings, innovative surface texturing, superfinishing, etc.), even greater fuel savings can be realized in the near future. Various polymeric materials have already been in use by the automotive industry for many decades (especially the interior section of vehicles). In recent years, there has been a strong push toward the development and use of carbon fiber-reinforced polymeric materials in other parts of vehicles for more effective weight reduction; however, these efforts are somewhat plagued by the relatively high cost of manufactured parts.

Considering the overarching needs for more fuel-efficient cars, in this chapter we aim to provide a critical review of the recently developed and emerging friction control technologies that can help save energy in passenger cars and reduce environmental pollution caused by CO₂ and other gaseous emissions. Specifically, we will attempt to provide a comprehensive overview of the recently developed and emerging coating technologies that can enable significant improvements in fuel efficiency and eco-friendliness of future transportation systems. Consistent with the scope of this chapter, the major emphasis is placed on coatings, but we will also summarize some of the more advanced surface and lubrication technologies that are important for overall efficiency, durability, and environmental compatibility of future vehicles.

For over a millennium, humankind has made great improvements toward achieving much more efficient and faster mobility. In the future, there is no doubt that this trend will continue and potentially lead to more advanced vehicles wasting far less energy yet delivering much higher power and producing much reduced CO₂ and other pollutants. In the following sections, we will first overview the impact of friction on energy and the environment and then concentrate on recent and emerging coating technologies that, when implemented, can further reduce friction and other parasitic losses and, hence, fuel consumption in engines.

1.2 Global Energy Consumption and Environmental Aspects

The energy production worldwide in 2011 was estimated to be about 13,113 million tons oil equivalent (Mtoe), which equals 549 EJ [20]. Of this, about one-third was consumed by the energy conversion and distribution sectors (i.e., power plants, furnaces, energy transfer or transmission lines, and energy usage), leaving only about 373 EJ for the global final energy consumption. This remaining part was distributed among the industry (29 %), the transportation sector (27 %), other energy users such

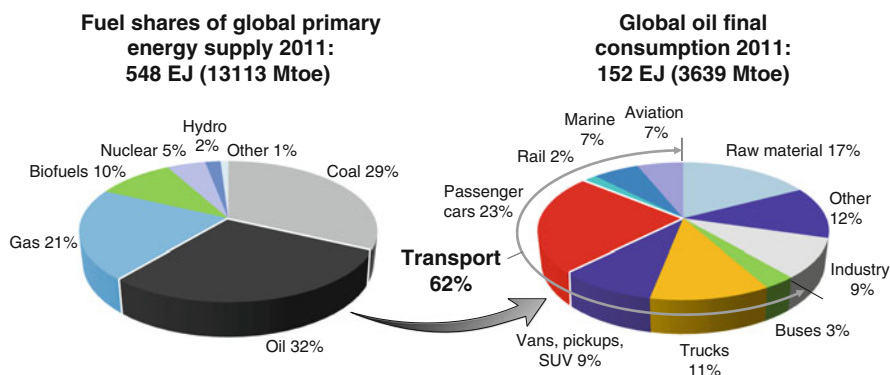


Fig. 1.2 Global energy and oil consumption 2011 [20]

as households and services (35 %), and nonenergy use (9 %). Crude oil is the largest part of the global energy supply (41 %), providing about 152 EJ, as shown in Fig. 1.2. Oil is also the main source of energy for the transportation sector, meeting 96 % of its energy needs.

The global emission of CO₂, the major greenhouse gas, has been steadily increasing over the years and recently reached a level of 31,600 Mt in year 2011 [21]. In the USA, the transportation sector accounted for 28 % of total greenhouse gas emissions, making it the second largest after the electricity sector in 2012. Overall, the worldwide transportation activities were responsible for 23 % of this amount (72,000 Mt), and the largest part came from road transportation. In year 2009, 71.7 % of all CO₂ emissions in Europe came from transportation vehicles on the road, 14.6 % from marine vehicles, 12.3 % from aviation, and 0.8 % from rail transportation [22].

1.3 Energy Consumption in Transportation

Transportation accounts for 63 % of the total global oil consumption. The rest is used by the industry for raw materials and other activities. The USA is the largest user of energy for transportation. Within the global transportation sector, road traffic is the largest user of energy (73 %) followed by marine (10 %), aviation (10 %), and rail (3 %) traffic, as shown in Fig. 1.3 [23]. However, ships are the largest carrier of world freight (75 %) followed by rail (13 %), road vehicles (12 %), and aviation (0.3 %) [24].

In terms of number of vehicles, road transport accounts for the largest amount of energy use within the transportation sector, mainly because of more than 1,000 million road vehicles rolling on the streets and highways (see Table 1.1). The main focus of this chapter is on road transportation, but for purposes of comparison, we also provide the energy uses by aviation, rail, and marine, as there are about 360,000 aircrafts worldwide, 120,000 trains, and 100,000 ships [25]. The number of aircrafts

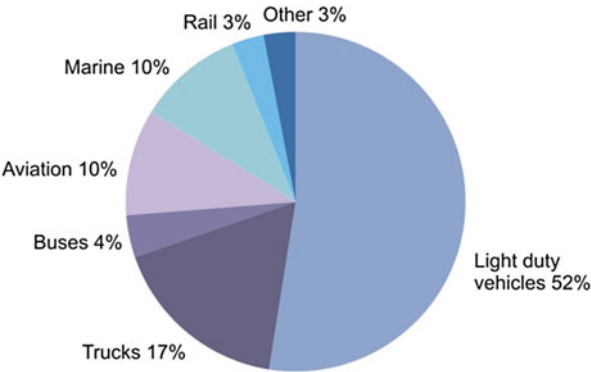


Fig. 1.3 Global breakdown of energy consumption by transportation vehicles [23]

Table 1.1 Global energy distribution per annum in transportation

	Road transport	Rail transport	Marine transport	Aviation (airline jets)	Total
Number of units worldwide	1,040 million	120,000	100,000	360,000	1,041 million
Energy use worldwide, EJ	67	3	9	10	93
Part of global energy consumption, %	18	1	2.4	2.7	25
Energy use for friction, EJ	22	1	3	1	30
Energy use for friction per transportation unit, GJ	21	8,300	30,000	2,800	NA

NA not applicable

and trains is well documented in statistical databases [26, 27], while the number of ships is more difficult to find because the definition is not as clear. There were 80,000 merchant vessels over 100 gross tonnage (GT) registered in 2011 [28]. In addition, there are almost 30 million pleasure boats and yachts of various types and sizes worldwide [29]. In our energy use comparison in Table 1.1, we have chosen to use 100,000 ships as representative for marine transport.

On average, 21 GJ is annually used by a road vehicle to overcome friction [7, 9]. We have estimated, based on available statistics, that annual energy use to overcome friction is 2,800 GJ for an average aircraft, 8,300 GJ for a train, and 30,000 GJ for a marine vessel (see Table 1.1).

1.3.1 Energy Consumption in Road Transportation

Road vehicles constitute the largest form of transportation, being dominated by about 700 million passenger cars and 300 million other light vehicles such as vans, pickups, and sport utility vehicles (SUVs), as shown in Table 1.2. In addition, there are

Table 1.2 Key figures for global average road vehicle per annum for friction and energy in 2011

	Single-unit trucks	Trucks and trailers	City buses	Coaches	Passenger cars ^a	Other light vehicles ^b	Road transport total
Number of units worldwide, millions	29.2	7.3	2.3	1.3	700	300	1,040
Average mileage, km	20,000	100,000	80,000	100,000	13,000	13,000	
Energy use worldwide, EJ	5.2	10.5	2.5	1.2	34	14	67
Part of global energy consumption, %	1.4	2.8	0.7	0.3	9.1	3.7	18
Energy use for friction, EJ	1.6	3.3	1.0	0.3	11.2	4.6	22
Energy use for friction per transportation unit, GJ	54	446	454	253	12	20	21

^aData from Holmberg et al. [9] corrected and updated to the situation in 2011

^bVans, pickups, and SUVs

29.2 million single-unit trucks, with a total weight over 3.5 tons, 7.3 million truck and trailer combinations, and 3.6 million city buses and coaches. The annual mileage is 13,000 km for light vehicles, 20,000 km for trucks, 80,000 km for city buses, 100,000 km for coaches, and 100,000 km for truck and trailer combinations. The data for passenger cars and trucks and buses were reported by Holmberg et al. [7, 9] while the data for other light vehicles are estimated on the basis of the passenger car data.

Annually, the passenger cars use about 11.2 EJ to overcome friction, while the combined vans, pickups, and SUVs use 4.6 EJ. The corresponding numbers are 4.9 EJ for trucks and truck and trailer combinations and 1.3 EJ for buses and coaches. The annual energy use per vehicle unit is the highest for city buses, truck and trailer combinations, and coaches, as seen from Table 1.2.

The breakdown of the energy use in an average passenger car on a global level is shown in Fig. 1.4. More than half of the fuel energy in an internal combustion engine goes to exhaust (33 %) and cooling (29 %), while the rest is transformed to mechanical power (38 %). Of the latter, the total frictional losses are the main part (33 %), while air drag (5 %) is a minor part. The largest sources of parasitic friction losses are those in the engine (11.5 %), in the transmission system (5 %), and from overcoming rolling friction of the tires (11.5 %). In addition, mechanical power consumed by friction losses in braking can be considered in such a way that deceleration energy can, on average, be considered as equal to the energy used for accelerating the vehicle. Thus, actually only 21.5 % of the fuel energy is used for moving the car consisting of the tire rolling resistance, the air drag, and the brake/acceleration energy, while the rest is energy losses.

The 33 % frictional losses (including rolling resistance and braking) are divided as follows: 35 % consumed by tire-road rolling contacts, 17 % by elasto-hydrodynamic contacts, 16 % by hydrodynamic contacts, 8 % in mixed lubrication contacts, and 2 % in boundary lubrication contacts. Viscous losses are 7 % and braking takes 15 % [9].

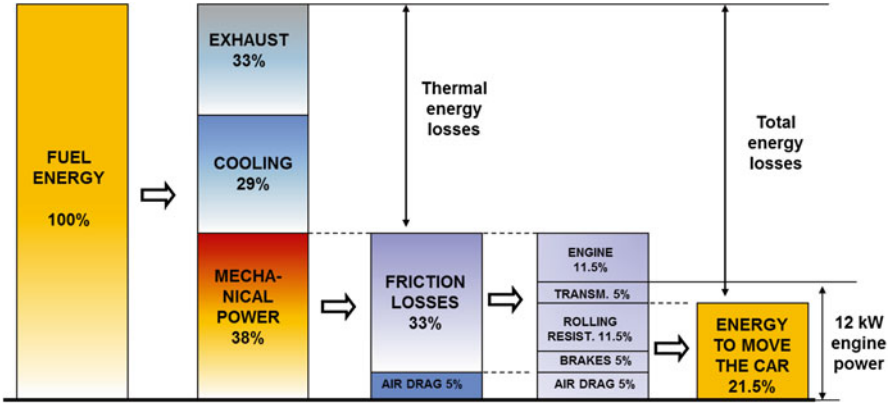


Fig. 1.4 Breakdown of fuel energy consumption in an average passenger car [9]

1.4 Potential Energy Savings and Emission Reduction

As discussed above, friction is a major energy consumer in transportation vehicles as it represents some 25–30 % of the total energy use. However, global efforts in tribological research have resulted in some breakthrough developments over the years, and there have been numerous reports that friction can be reduced by as much as 90 % from the levels found in earlier vehicles [7, 9]. Figure 1.5 shows this trend as estimated for the different tribological contact and friction mechanisms in heavy-duty vehicles over the years 2000–2025. Some of the technological breakthroughs behind such reductions are discussed in Sect. 1.5.

Holmberg et al. [7] calculated that by implementing the most advanced tribological solutions in modern commercial heavy-duty vehicles of today worldwide, the energy consumption due to friction could have been reduced by 37 % (see “truck and bus 2013” in Fig. 1.5). Furthermore, if the best tribological solutions demonstrated in research laboratories were implemented, energy consumption would have been further reduced (see “laboratory 2013” in Fig. 1.5), and if the new solutions forecasted for 2025 were fully implemented, the energy consumption due to friction would be reduced by 68 % (see “truck and bus 2025” in Fig. 1.5). Note that the savings in fuel energy may even be larger than the total energy used to overcome friction because reduced friction results in reduced energy demands, and thus the energy going to exhaust and cooling is also reduced.

Obviously, implementing today’s advanced tribological solutions in all trucks and buses would require an enormous effort and would result in major design and manufacturing changes and large implementation costs, which cannot be commercially justified at present. Nonetheless, it would be realistic to estimate that perhaps half of this level could be reached in the short term, i.e., within 4–8 years, by means of large-scale research, development, and implementation efforts leading to new tribological solutions in engines, transmissions, brakes, and tires, which can potentially result in about 14 % overall reduction in fuel consumption.

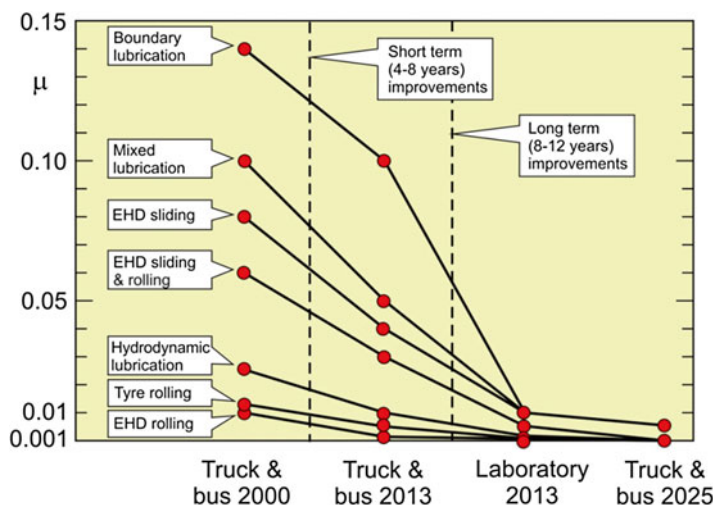


Fig. 1.5 Trends in coefficient of friction reduction in four truck and bus categories for different lubrication mechanisms and for rolling friction. *EHD* electro-hydrodynamics [7]

Table 1.3 summarizes potential energy and economic savings as well as emission reductions [7]. The data indicate that there are more than 1,000 million road vehicles using about 22 EJ fuel energy annually to overcome friction and other parasitic losses. In the short term (4–8 years), on average, 17.5 % of the energy consumed by friction could be reduced by efficiently implementing new technological solutions. On an annual global basis, this level of energy savings would result in an economic savings of 475,000 million euros and reduced CO₂ emissions of 856 million tons.

1.5 Coating Technology for Improved Fuel Efficiency

To meet the increasingly more stringent operational conditions, tighter emission control standards, and increased fuel efficiency and durability demands of future vehicles, a great deal of effort has been directed toward the development of low-friction materials and coatings in recent years [3–6, 30, 31]. At present, there exist some super-low-friction materials that can provide friction coefficients in the super-lubric sliding regimes, i.e., less than 0.01. Their wear rates are also extremely low. Figure 1.6 shows typical friction and wear values of some of the emerging and more typical engineering materials while Table 1.4 provides a list of some of the coatings that are already used in various engine components. As is clear, there are not many engineering materials that can provide the levels of friction and wear coefficients that we desire for engine and other applications. Consequently, the use of liquid lubricants is a must for achieving low friction and wear.

As mentioned above, equally intense R&D efforts are underway in lubricant and additive areas as well. Together, these efforts are expected to provide much lower

Table 1.3 Potential energy and economic savings and CO₂ emission reduction per annum as a result of implementing new tribological solutions in road transport

	Single-unit trucks	Trucks and trailers	City buses	Coaches	Passenger cars ^a	Other light vehicles ^b	Road transport total
Short-term saving period, years	4–8	4–8	4–8	4–8	5–10	5–10	5–9
Short-term savings/reduction, %	12	15	11.5	15	18.5	18.5	17.5
Energy savings from reduced friction in short term, EJ	0.62	1.6	0.29	0.18	6.3	2.6	11.6
Cost savings from reduced friction in short term, 1,000× million €	24.4	61.7	11.3	7.1	260	110	475
Fuel savings from reduced friction in short term, 1,000× million liters	17.5	44.1	8.1	5	178	73	326
CO ₂ savings from reduced friction in short term, million tons	45.9	116.0	21.2	13.3	468	192	856

^aData from Holmberg et al. [9] corrected and updated to the situation in 2011

^bVans, pickups, and SUVs

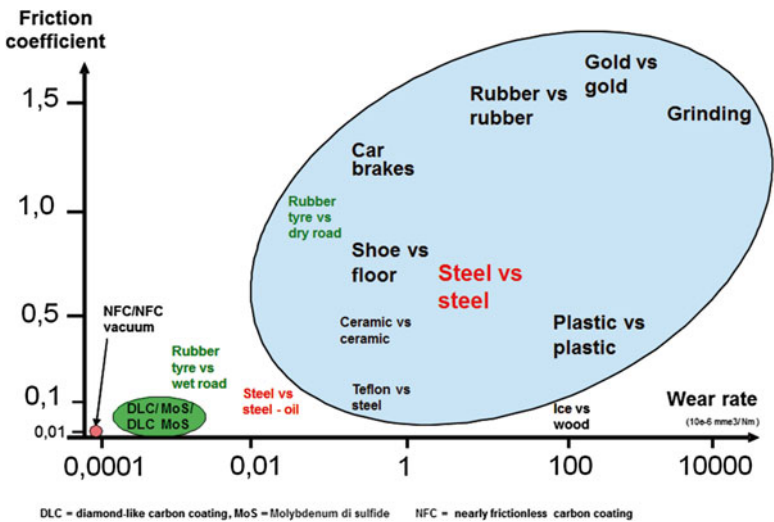


Fig. 1.6 Typical friction and wear coefficients of some materials, coatings, and special operations

Table 1.4 Examples of coatings for vehicle applications

Application	Coating	Thickness μm	Substrate	Counter-surface	Improvements
Sliding bearings	DLC, CrN, WC-C, CrN/CrCN/DLC	5–50	Steel	Steel	Up to 7 times reduced wear rate. Decrease in friction
Rolling bearings, gears	DLC, MoS ₂ , Pb, Co, Cr, Au, PTFE, ML, DP	0.05–3, optimum typically 0.2–1	Steel	Steel	Increased fatigue life by up to 10 times. Reduced friction
Gears/driveline components	WC/C, B4C, TiN, DP, TiC, AlMgB ₁₄	1–10	Steel, carburized/case-hardened steel	Same as substrate or coated	Reduced friction and wear. Up to 70 % torque capacity increase. Increased lifetime by 3 times
Piston assembly	CrN, CrC, Cr-a-C, Cr, Mo, MoN, DLC, Nikasil, graphite, Doped MoS ₂ , Ni-P, Zinc Phosphate	10–50	Cast iron, carburized/case-hardened steel, aluminum	Steel, cast iron, Al and Ti alloys	Increased lifetime in rings; reduced friction and wear; protection against scuffing and corrosion/oxidation
Fuel components	TiN, CrN, TiCN, DLC, WC, TiC,	0.5–2	Steel, nitrided/carburized/case-hardened steel	Metal and ceramic debris, sand, dust, rocks, TiO ₂	Protection against wear, corrosion, and scuffing. Improved lubricity, reduced varnish, and deposit formation
Sacrificial/break-in coatings	MoS ₂ , graphite, zinc and manganese phosphate, PTFE	1–10	Steel, cast iron, aluminum	Same as substrate or coated	Controlled/mild wear in the beginning. Increased load-bearing capacity and reduced friction
Heat resistance/thermal barrier	Many gradient coating involving ZrO ₂ , Y ₂ O ₃ , Al ₂ O ₃	50–500	Cast iron, steel	Steel, Al- and Ti- alloys	Low-heat rejection, protection against oxidation and thermal/mechanical degradation
Dry lubricant	DLC: a-CH ₃ , or a-CN, PTFE, graphite, MoS ₂	1–20	Steel, aluminum, polymers, plastics	Same as substrate or coated	Reduced wear and corrosion for flexible joints, door hinges, lock-in systems
Coatings for non-engine applications					

ML multilayer coating, DP duplex coating

friction and wear than before, despite more stringent or demanding operating conditions of new vehicles. In particular, the use of lubricious coatings on critical engine parts has grown dramatically in recent years, mainly because they have the ability to substantially increase the load-bearing capacity and lubricity of contact interfaces. This improvement is mainly due to higher mechanical hardness and strength and shearing, easily occurring under boundary-lubricated sliding conditions. Due to modified surface thermal properties, lubricious coatings may also improve performance under elasto-hydrodynamic and hydrodynamic lubrication [32]. Nowadays, these coatings are applied on all kinds of engine parts by means of advanced physical and chemical vapor deposition (PVD and CVD) methods. Among other materials, the use of DLC has exploded in recent years, and this material is being applied on hundreds of millions of engine parts and components annually [31, 33–36]. Owing to their self-lubricating nature, DLCs can act as a backup lubricant in oil-lubricated contacts to provide much lower friction, even under severe boundary and oil-out conditions [37–39]. Modern PVD and CVD systems used in the production of these coatings can handle thousands of parts on each deposition run at reasonable costs [40, 41].

Under boundary-lubricated rolling or sliding contact regimes, where direct metal-to-metal contacts occur, certain DLC coatings (especially the tetragonal amorphous carbon, or ta-C) are able to dramatically lower friction and protect contacting surfaces against wear and scuffing. Likewise, for engine oil lubrication with slip-rolling conditions and extreme pressures, it was shown that ta-C coatings perform much better than other types of DLC coatings [42].

As with other engineering surfaces, DLCs interact with the additives in oils to form either more protective boundary films or suffer accelerated wear and higher friction [43–46]. Under extreme pressures, the mechanical properties of DLC coatings are very important, and only those coatings with adequate hardness could survive. Under lower contact pressures, a high fraction of sp^2 -bonded carbon was more advantageous for wear reduction under boundary lubrication [47]. Fullerene-like DLC films on common rail fuel systems were shown to improve fuel economy by 1.5 % and reduce emission by 2–5 % [48].

Under hydrodynamic and mixed-boundary lubrication conditions, the effect of coating could be marginal, but if the type of DLC deposited on the surface is also oleophobic (i.e., non-wetting to lubricant), it may still help reduce some of the shear or drag forces and thus may have some beneficial effect. Overall, with the use of lower-viscosity engine oils, greater burden has been placed on DLC and other coatings for not only reducing friction but also protecting surfaces against wear and scuffing. Recent studies have confirmed that indeed, with the use of hard- and low-friction coatings, the fatigue lifetime of gears and other heavily loaded rolling contact bearings can be altered substantially [49]. In certain cases, rolling contact fatigue life has been increased as much as tenfold with the use of hard coatings [3, 50]. In the case of gears, sevenfold increase in wear resistance has been reported, and such an improvement has led to threefold increase in gear life [51]. Similar improvements

have also been reported for multilayer Cr/CrN- and CrN/ZrCrN- coated gears under extreme pressure conditions, even in the presence of NaCl, which otherwise triggers tribocorrosion [52]. Silicon doping of DLC was found to increase wear resistance but not improve friction [53].

Considering the severity of the tribological and environmental conditions of future engine systems, further improvements on either the coating or the lubricant may not be adequate. Instead, a surface engineering approach involving combining surface texturing with coatings may be far more effective [54]. It has been shown that when textured Si-DLC coatings are tested under lubricated sliding conditions in the temperature range of room temperature to 200 °C, friction coefficients and wear rates are much lower compared to those of the untextured Si-DLC coatings. With the development and use of multilayered coatings of CrN/CrCN/DLC, the performance and durability of fuel injectors have been dramatically improved [55]. In other studies, CrC/a-C:H coatings performed better in the presence of MoDTC as opposed to conventional DLCs, which were otherwise shown to adversely interact with this additive in the oil [56].

Engines, drivetrains, and transmissions have many types of rolling, sliding, or reciprocating components. Among others, the most important tribocontacts giving rise to frictional losses include piston rings and cylinder liners, gears, bearings, valves, and cam and shim contacts. Components like fuel injectors, commutators, ball pivots, connecting rods, piston pins, synchronizer rings, clutch mechanisms, shifter forks, flexible joints, shock absorber parts, steering system parts, and brake components may also contribute to overall frictional losses but at much reduced levels [57, 58]. Since all of these components are in use for a very long time, total accumulated frictional losses could still be significant; hence, currently, a systematic effort is underway to reduce friction even in such components.

In the past, weaker adhesion between top coatings and bottom substrates had posed some reliability and liability issues, but the more advanced PVD technologies that are in use today employ pulse DC, arc-PVD, and high-power impulse magnetron sputtering (HIPIMS) to overcome such problems. Furthermore, interface engineering has greatly advanced in recent years, and the transition layers at the coating/substrate interface are strategically selected to provide not only very strong bonding but also to act as a buffer for thermal expansion mismatch and residual stress buildup that could otherwise trigger delamination under the cycling loading and unloading motions that most engine components experience. Researchers in the field have developed and used sophisticated computer codes and finite element methods [59, 60] to predict coating performance and durability under severe loading. With the use of such methods, they were able to more closely match the coating properties with those of the substrate materials and thereby avoid premature delamination and fracture under severe operating conditions. Overall, current PVD and CVD techniques are providing much superior chemical and structural qualities to coated engine parts, leading to long endurance lives and lower friction coefficients than ever before, even under marginally lubricated sliding conditions [61].

DLC and other low-friction coatings such as MoS_2 are intrinsically lubricious and, hence, can reduce friction of dry sliding contacts by more than 90 %. Due to its very soft nature, MoS_2 is not used as a primary tribological coating in engines, but DLC is now widely used as an overcoat in numerous engine components. It is much harder than MoS_2 and could even be made super hard if needed. Due to its many variants and flexibility in chemical and structural design, among all functional coatings that we have today, DLCs have attracted the greatest attention in recent years. Compared to other coatings, DLCs can provide some of the lowest friction and wear coefficients under both dry and lubricated conditions [62]. Systematic studies by Kano et al. [63] have shown the possibility of reducing boundary friction by as much as 90 % with tetragonal amorphous carbon (ta-C) in the presence of some polar additives like glycerol or glycerol monooleate. In fact, much lower friction appears possible with the use of different types of additives in combination with low-friction coatings like DLC. The addition of friction modifier additives like glycerol monooleate to a poly-alpha-olefin oil gave a friction coefficient of 0.05 in sliding contact with ta-C. However, the same material combination had a coefficient of friction of 0.005 when lubricated by pure glycerol [64–66]. This friction coefficient is about one-tenth of what currently can be achieved with the best lubricating oils. At present, ta-C coatings are routinely applied on valve-train components, piston rings, and pins in huge quantities [67].

Besides ta-C, nano-alloyed or doped DLCs have also made a strong entry into automotive applications. In particular, Si-doped DLCs have been tried in various engine applications, and significant improvements in friction and wear have been reported under boundary-lubricated sliding regimes. Podgornik and Vizintin [68–69] reported that W-doped DLC coatings reduce boundary friction by more than 30 % compared to uncoated steel/steel contacts. In another study, Gåhlin et al. [70] reported 70-fold improvement in the lifetime of WC/C-coated gears when tested in an FZG test machine. Some of the other coatings that have been used in engines for friction and wear control include hard chrome, CrN, AlMgB_{14} , WC/Co, AlTiN, W-C:H, $\text{AlMgB}_{14}\text{-TiB}_2$, and a variety of thick coatings applied by various thermal and/or plasma spray processes [61, 71–77]. CrN-based thick coatings are still used extensively in piston rings and some other components like tappets.

In addition to coatings, various surface engineering approaches are used to control engine friction and wear. Among others, surface texturing has attracted the greatest attention in recent years. Honing is a well-controlled texturing practice for ring-liner assemblies and has been used by industry for many years, although the laser surface texturing of rings and liners has been shown to reduce fuel consumption of engines by as much as 4 % [78–81]. These dimples are in the form of shallow (10–20 μm deep) craters with about 100 μm diameter. They can serve as reservoirs for lubricants and thus increase the hydrodynamic lubrication efficiency of textured surfaces. Furthermore, dimples can effectively trap wear debris or third-body particles generated at sliding interfaces and thus reduce wear. Overall, when such optimized dimples are produced on engine and drivetrain components, one can expect much improved fuel economy due to reduced friction or torque, while reduced wear translates into longer wear life and thus increased durability.

1.6 Discussion

In this chapter, we have drawn attention to friction- and wear-related energy losses, environmental issues, and some of the existing and emerging coating technologies that can offer low-friction and high wear resistance under demanding tribological conditions. Globally, huge amounts of energy are lost to overcome friction and wear in various transportation systems. In passenger cars, only about 20 % of the total fuel energy is actually used to move the vehicle. Environmental burdens created by such high energy waste are also enormous and suspected to cause climate change. To reduce the severity of such adverse energy and environmental impacts, researchers have been working to develop low-friction materials, coatings, and lubricants. In particular, the uses of low-friction coatings such as DLC have increased tremendously in recent years and now become an integral part of many engine applications.

So far, mostly “simple-structured” DLC films with monolithic phase have prevailed and continue to enjoy increased attention. These coatings consist of a single layer that is made of hydrogen-free and hydrogenated DLCs. Occasionally, a few alloying elements like Si, W, and Cr are added to enhance mechanical, thermal, and tribological behavior. Multiple layers containing more than one type of DLC or other hard nitrides and carbides have been tried in laboratories, but only a few engine applications have adopted such coatings for better friction and wear control. The most desired processes for applying such coatings are commercially mature PVD and CVD with a huge capacity and, hence, lower cost per piece. The most successful coatings for engine use include a variety of DLC films (in particular, ta-C type) and CrN. More exotic coatings like WC/C, AlMgB₁₄, WC/Co, AlTiN, W-C:H, AlMgB₁₄-TiB₂, CrC, and many others presented in this book hold high promise to provide much superior friction and wear performance and may be used in large quantities in future engine applications.

For all of the coatings mentioned above, strong adhesion to substrate materials is a must for long service life and functionality. In most engine components, these coatings undergo cyclic loading and unloading; if the interface adhesion is not strong, they often delaminate and undergo accelerated wear due to third-body wear triggered by chipped or worn coating particles. Modern deposition systems (like PVD and CVD) are capable of providing strong bonding between top coatings and their substrates. With the development and uses of more advanced methods like high-power impulse magnetron sputtering, these coatings have achieved much superior adhesion, and most often they remain intact for the duration of a test or specific application. For engine applications involving high temperatures (such as piston rings), the type of coatings has to be selected very carefully. Some of the DLCs (especially the hydrogenated ones) are not thermally stable and, hence, may wear out in the long run. The ta-C and Si, Cr, and Ti-doped DLCs may work better for such applications. For a very long time, hard Cr and CrN coatings were the preferred coating types for piston ring applications, mainly because of their higher thermal and oxidative stabilities. Multilayered and gradient coatings

involving CrN, CrCN, and DLC are being developed and are expected to afford greater multifunctionality and lubricity over broader temperature ranges.

By and large, DLC coatings account for the great majority of all coatings in engine use today. Other functional coatings are also making a strong entry into industrial fields, as operating conditions are becoming much harsher. In particular, multilayer nitride and carbide layers that also incorporate a DLC film are also being used as protective, low-friction coatings where severe thermal and mechanical loadings are the major considerations. In short, functional PVD and CVD coatings have been around for a long time, and they have been meeting some important and critical tribological needs in engines. There is no doubt that with the development and use of more advanced methods, these coatings will attain much higher multifunctionality and, hence, superior performance and durability in more demanding tribological applications.

1.7 Summary and Future Directions

The operating conditions of future engines are envisioned to become far more stringent, and hence, the development and uses of more effective friction- and wear-resistant materials, coatings, and lubricants will become obligatory. Among the major drawbacks of current engine materials and lubricants are that they cannot provide the low levels of friction and wear that are needed over broad temperatures, environments, and other conditions.

In the future, what will be desirable is that the coating applied on an engine component is able to provide additional functionality when needed to meet the changing requirements of an engine operating condition. Design and synthesis of such smart coatings require deep knowledge of the often changing operational requirements of an engine, as well as the types of film structure and chemistry that can meet such requirements, including temperature, contact pressure, and other environmental conditions. For these, composite coatings which also incorporate additional surface texturing may be needed. Coating systems (e.g., WC/DLD/WS₂) have been developed in the past and shown to provide self-adaptation to operating conditions involving humid, dry, or vacuum environments of spacecraft [82]. One of the major challenges for future engine systems will be to achieve and maintain adequate lubricity between sliding or rolling components that will be exposed to temperature and pressure extremes, as future engine systems are expected to be far more compact and possess much higher power density than before. When such trends are combined with increasingly less viscous oils (down to perhaps 0W8 to 0W16 grade levels), the contact severity and, hence, the wear load indexes will undoubtedly rise. Even the best self-lubricating coatings, including DLCs, may not be good enough to provide the long life and good performance that we desire. Accordingly, in the near future, much superior coatings that can operate over a broad range of load, speed, and temperature will be needed. One of the major shortcomings of certain DLCs used in engine applications is gradual structural change under higher thermal and mechanical loadings,

leading to accelerated wear. Again, the future challenge is developing smarter coatings that can quickly adapt to changing operational conditions of an application without much degradation in structure, performance, and property.

Overall, from a tribological point of view, what will be the most desirable scenario for future engine systems is that the tribological materials, coatings, and lubricants last for their projected lifetimes with little or no preventive maintenance or oil change. In some transmission and driveline gearbox systems, this scenario has already been achieved. Some drivetrain components in diesel engines already last more than a million miles before the need for replacement or a major overhaul. Similar durability and performance targets can also be achieved in other engine components by the development and implementation of more advanced coating and lubrication technologies. Undoubtedly, there is no single or simple (either material or lubricant) solution to the long-term durability problems in most critical engine components (piston rings, tappets, fuel injector plungers, etc.), and hence, these will have to be targeted for novel and smarter coatings. Otherwise, with the demands posed by harsher conditions year after year, they may experience more frequent failures. In short, in the near future, more effective materials, coatings, and lubricants will be needed to keep pace with the higher efficiency and durability demands and lower emission targets than what have been feasible so far.

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Chapter 2

Diverse Coatings for Engine Parts

Sung Chul Cha

Abstract The focus of recent attention in automotive field is on low friction and wear resistant coatings (e.g., (Si-)DLC, TiAlCrSiCN, polymer) for use in powertrains and thermal spaying applications. As a future perspective, the development of advanced coating materials and processes will be steadily required to enhance quality and functionality of parts being coated and to reduce process time and cost. Concerted research effort converging coatings with surface patterning and finishing is necessary to maximize the overall functionality and performance of engine parts.

Keywords Fuel efficiency • Low friction • Wear resistance • DLC coating • Engine parts • Transmission parts • Si-DLC • PTFE coating • TiAlCrSiCN • High temperature parts • Thermal spraying • YSZ • Mo spraying • Advanced coatings

2.1 Introduction

Improving efficiency and protection of environment are currently the megatrends for automotive-related industries. Their main object is to achieve competitive capability in terms of fuel efficiency and exhaust gas regulations. Diverse companies focus on the R&D in eco-friendly technologies with keywords, e.g., new ecosystem preservation (Arthur D. Little), environment and climate protection (Bosch), environment (Continental), green (Delphi), and safety and environmental regulation (Ernst and Young). Until 2020, CO₂ emission of 50 g/km shall be achieved with vehicles in hybrid, electric, fuel cell system and with alternative fuels including biodiesel, ethanol, LPG, and CNG. For 2020, the market share of eco-friendly vehicles from diverse companies and institutions (Bain, BCG, Deutsche Bank, McKinsey, Credit Suisse, Bosch, J.D. Power) is predicted to be 6–40 % hybrid, 2–10 % EV/FCEV, and 50–92 % internal combustion vehicles [1]. Furthermore, for 2025, CAFE (Corporate Average Fuel Economy)-mandated fuel economy has to

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reach 54.5 mpg, i.e., 23.2 km/l with yearly improvement of 3.8 %. There are diverse techniques to improve the fuel economy, e.g., combustion with high compression, variable valvetrain, high-speed transmission, idle stop and go, optimal body design, active air flap, and active rear end flow control in vehicles. Surface engineering and coatings play an important role in numerous automotive applications. They are responsible for the development of low friction and highly durable mechanical parts especially in engines, transmissions, as well as interior and exterior parts. In the following, some of these will be discussed in details.

2.2 Low Friction and Wear Resistant Diamond-Like Carbon Coating

To reduce the wear of materials, key factors to consider can be high mechanical hardness or strength, low friction coefficient, and low surface roughness. DLC (diamond-like carbon) is a well-known coating and widely applied on numerous automotive parts to achieve low friction and high wear resistance. DLC is predominantly applied on parts by physical or chemical vapor deposition processes using a variety of carbon sources including solid graphite targets as well as hydrocarbon source gases (such as C_2H_2 , CH_4). DLC is a mixture of graphitic and diamond-like phases with or without hydrogen and other doping elements for special performances, e.g., F-, Si-, and W-doped DLC for controlling surface energy, reactivity, and thermal stability [2].

In this work, applied DLC for engine parts is composed of $sp^2:sp^3$ ratio of approx. 2:3 with 5–12 at. % hydrogen, and it has minimum hardness of 3,000 HV, minimum adhesion of 30 N (in scratch test), surface roughness of R_a 0.04 μm , and friction coefficient of about 0.05 under oil-lubricated sliding conditions. DLC coating has layer design of minimum 0.5 μm thick Cr and W-DLC or CrN as buffer layer and minimum 1 μm thick DLC as top layer. Substrate is carbonitrided CrMo steel (SCM415, 16MnCr5) with surface hardness of minimum 700 HV with effective case depth of 500 μm . DLC-coated tappets could enhance the friction reduction by 40 % leading to the fuel economy improvement of 0.6–0.8 %. Figure 2.1 shows PVD and PACVD coating machine with capacity of 7,500 tappets for DLC coating per batch.

Tribological performance of DLC is influenced by hydrogen, humidity, and temperature. Especially, the friction coefficient and wear rate of hydrogenated DLC increase by the increase of humidity and temperature. By increasing the temperature, hydrogen in DLC effuses outwards and DLC film graphitizes, resulting in the reduction of film hardness. Donnet and Erdemir reported that hydrogenated DLC begun to wear above 147 and at 250 °C wear accelerated dramatically. In order to improve the properties of hydrogenated DLC, alloyed DLCs were considered with the following advantages: aluminum addition for increase of layer toughness and silicon for reduction of compressive stress and thermal stability. It enables low and stable friction performance and increase of graphitization temperature [3]. Friction behavior of DLC and Si-DLC was investigated with various engine oils by Ford/Fraunhofer [4]: the results showed that Si-DLC is a good fit for modern engine oil

Fig. 2.1 PVD machine for DLC-coated tappets

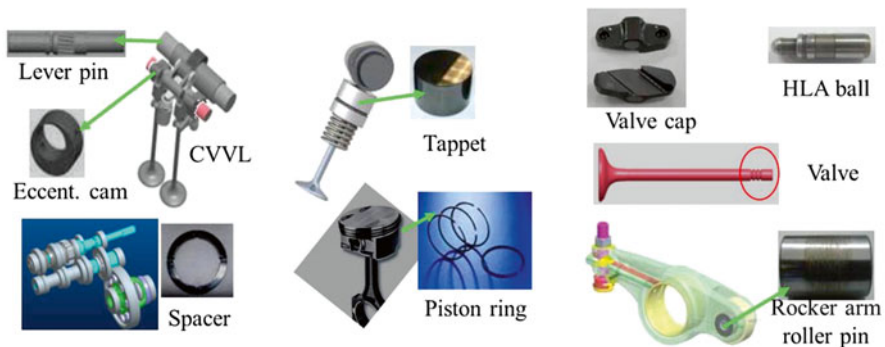


Fig. 2.2 DLC-coated parts for engine and transmission (Si(O)-DLC for tappet, piston ring, valve, rocker arm pin)

which contains Mo and Zn addition for low friction and long-wear life. Toyota mentioned that the wear performance of DLC can be adversely affected by Mo-DTC (molybdenum-dithiocarbamates) because during sliding, MoO_3 is formed and degraded DLC structure [5].

Si-DLC with 4 at. % Si provides low/stable friction performance with Mo-DTC oil. Formed Si-rich oxide debris (hydrated silica) or Si-O-O-H protect DLC from MoO_3 attack [3].

To improve the DLC's thermal stability and sticking resistance, silicon is used as an alloying element widely by industry at present. A variant Si(O)-DLC is coated by plasma-assisted CVD with HMDSO (hexamethyldisiloxane) or TMS (tetramethylsilane) precursor. Si-DLC has lower hardness of 2,500 HV (vs. DLC), but it has good thermal resistance up to 400 °C and low adhesion or sticking behavior due to low surface energy [2, 3, 6].

Figure 2.2 shows some engine parts of DLC by PVD and Si(O)-DLC PACVD sputtering coatings for low friction and improved durability. Lever pin and eccentric

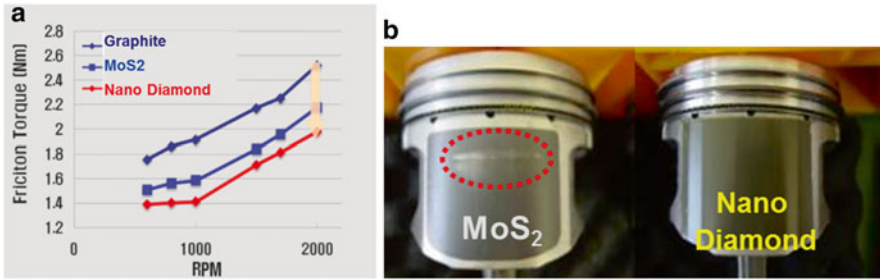


Fig. 2.3 Friction reduction of nanodiamond PTFE coating (a) and wear comparison after (b) engine test

cam were coated with DLC with the effects of 0.2 % fuel economy and NVH improvement. Spacer in manual transmission was DLC coated with significant durability improvement and cost savings regarding substitution of expensive high-grade alloy. Tappets and piston rings were Si(O)-DLC coated with 0.6 %, 0.3 % fuel economy each and durability improvement. For diesel engine valve cap, hydraulic lash adjuster (HLA) ball, intake and exhaust valve tip, and rocker arm roller pin were also coated with DLC and Si(O)-DLC. Especially rocker arm roller pin was Si(O)-DLC PACVD sputtering coated at low temperature, i.e., 150 °C, which is lower than substrate tempering temperature of 180 °C. General DLC PVD sputtering temperature of 200 °C led to size change or deformation of part [7].

As a main moving part in engine, piston skirt coating is very important to enhance fuel economy. Currently graphite or MoS₂ is coated on piston skirts. MoS₂ with PAI (polyamide-imide) and graphite can improve fuel economy by 0.3 % vs. graphite. In this work, we developed PAI and PTFE coatings with 2 % of nanodiamond particles in them, and these composite coatings could enhance fuel economy by 0.3–0.4 % (vs. MoS₂). In particular, nanodiamond PTFE composite coating could reduce friction torque by 7 % vs. MoS₂ and 21 % vs. graphite (Fig. 2.3). And after engine durability test, it has proven to provide excellent wear resistance compared to other coatings.

2.3 TiAlCrSiCN Coating for High-Temperature Parts

Exhaust gas recirculation (EGR) is composed of flap valve, shaft, bushes, washer, and housing. Actuator controls the opening of flap valve. During flap valve opening, flap valve and bushing rub with each other. As a result, EGR flap valve and shaft can be worn, resulting in adhesive and abrasive wear and following engine warning, noise, and lack of power. After an engine durability test, it was determined that valve wear depth was 1.1 mm and shaft was also attacked by adhesive and abrasive wear (Fig. 2.4). To prevent these EGR wear problems, washer is added between valve and bushing, but this action did not revise the wear problem effectively enough. These parts work at 650 °C and need high resistance to thermal, wear, adhesive degradations, and at the same time, they have to provide low friction to

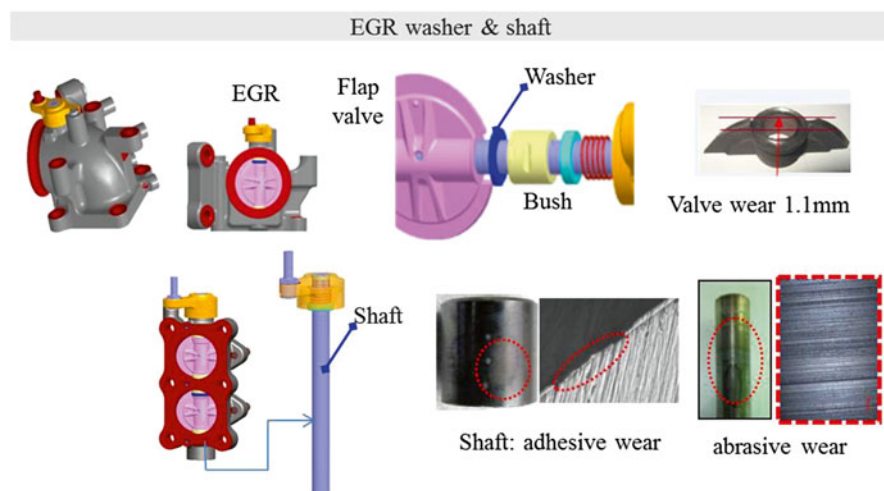


Fig. 2.4 Wear problems of EGR valve and shaft

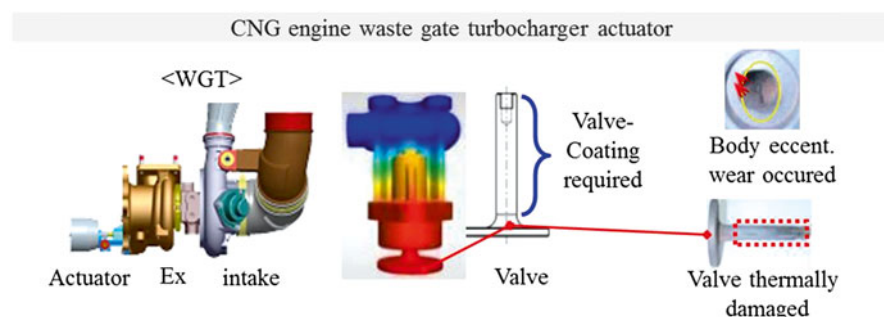


Fig. 2.5 Wear problems of turbocharger actuator valve body

each counterpart. As a similar problem, valve body, inside of turbocharger actuator of CNG (compressed natural gas) engine, is eccentrically worn, believed to be caused by the sliding motion of valve. This has led to engine power drop (Fig. 2.5). Therefore, in turbocharger actuator, material of valve body is changed and cooling system was optimized, but the problem was reversed or revised effectively enough.

To prevent costly and time intensive durability tests, high-temperature friction tests for coatings in heavy duty engines were carried out. A total of four coatings and the baseline material were compared with high-temperature friction tester at Korean Institute of Ceramic Engineering and Technology (Fig. 2.6). Tester is Multi-Purpose Wear Test system (model NEO-TRIBO MPW 110, Neoplus Co.). Test condition was 650 °C, 30 N loads, 2 km, and 6 h. As a result, maximum thickness of worn area was 65 μm by current material. By comparison of worn depth and mass, TiAlCrSiCN was ten times more wear resistant than the baseline material and

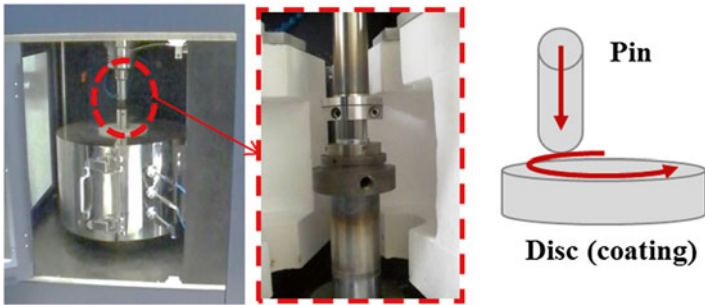


Fig. 2.6 High-temperature friction/wear test-plate on disc (condition: 650 °C, 30 N, 2 km, 6 h)

Table 2.1 Results of high-temperature wear and friction test-candidate coatings for washer

Candidates	Current: SUS420J2	CrN	CrTiSiN	TiAlCrN-CrON	TiAlCrSiCN
Wear depth (μm)/image	65 	13 	8 	8 	0 

Table 2.2 Results of high-temperature wear and friction test-candidate coatings for EGR valve

Candidates	Inconel 713C	CrN	TiAlN	CrTiSiN	TiAlCrSiCN
Coating-disc wear (mg)	15.1	7.5	2.3	2.2	1.48
Counterpart-pin wear (mg)	120.3	51.2	29	32	17.1
Friction coefficient	0.85	0.63	0.69	0.72	0.42
Adhesion/sticking resistance	Low	Middle	Middle	High	High

showed four to eight times better performance than other coatings tested as can be seen in Table 2.1. Based on this result, wear problems could be solved without application of high cost superalloy, e.g., Inconel.

To determine the appropriate coating type for EGR valve, the baseline material and four coatings are tested by high-temperature pin on disc machine. Coatings were prepared as disc and friction counterpart as pin (EH51HRD, sinter materials with high density for high-temperature application). Test condition was 700 °C, 20 N, 2 km, and 0.1 m/s in air. As a result, maximum weight loss was 135.4 mg by baseline material and pin. TiAlCrSiCN was approx. 7 times more resistant than the baseline material and showed 1.8–3.2 times better performance than other coatings tested as can be seen in Table 2.2. Furthermore, their excellent anti-sticking behavior was qualitatively proven.

TiAlCrSiCN-coated washer is tested for 300 h in a long durability test in vehicle. The wear depth was only 0.08 μm (vs. CrN 9.6 μm) with improvement of 120 times. In addition, TiAlCrSiCN-coated valve of CNG engine turbocharger is tested and compared with other coatings. Extreme durability test of engine was carried out at 670 °C and the actuator valve operated 135,000 times (Fig. 2.7). It showed

Fig. 2.7 Engine test—CNG engine turbocharger actuator

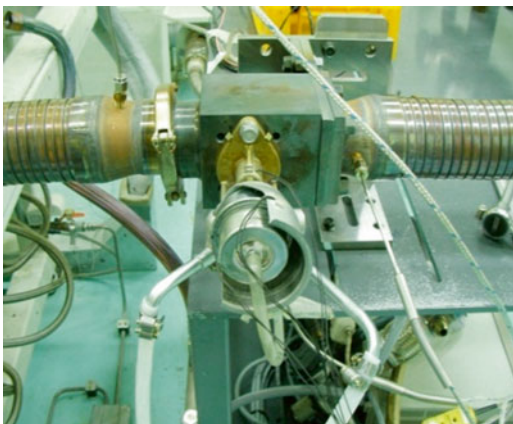


Fig. 2.8 TiAlCrSiCN-coated parts for production (EGR washer, shaft, actuator valve)

excellent results: wear depth was 30 μm , five times better than others with 150 μm wear depth.

Figure 2.8 shows the TiAlCrSiCN-coated parts for production. The application of TiAlCrSiCN coating in EGR washer is expanded for two heavy duty engines. This application led to significant cost reduction and contributed to the increase of market share in truck and bus business. Furthermore, this coating enhanced the wear resistance of high-temperature friction parts and secured the coating technology for high-temperature application by coping with EURO 6 or 7 regulations.

TiAlCrSiCN is coated with Cr/CrSi/TiAl targets and Ar, N_2 , C_2H_2 gases in a coating chamber under vacuum atmosphere (Fig. 2.9). Firstly, chamber is heated up to 450 $^\circ\text{C}$ and then CrN is formed with Cr target and N_2 gas and subsequently TiAlN/CrN multilayer with TiAl, Cr targets, and N_2 gas. And then all targets and gases took part in the generation of TiAlCN/CrSiCN nano-multilayers.

2.4 Thermal Spraying and Advanced Surface Engineering

Currently, plasma-based CVD and PVD methods have been used mostly to produce thin DLC and other coatings in order to enhance fuel efficiency of vehicles, but these techniques could be rather cost intensive. To reduce the cost strain, thermally

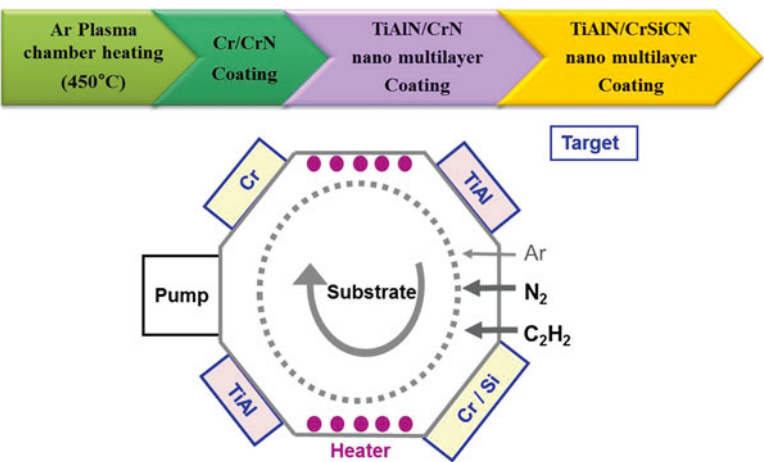


Fig. 2.9 Coating procedure and schema of TiAlCrSiCN

Table 2.3 Friction behavior of Mo-sprayed samples in oil and dry condition

Mo-sprayed samples	CoF	Roughness Ra (μm)		Thickness (μm)	Hardness (GPa)
		As received	Polished		
Oil (GF4)	0.050	0.9998	0.5134	50	13.2
Dry	0.615	1.1994	0.5564	75	12.6

sprayed coatings are substitutive candidates for achieving lower friction. They can also act as thermal barrier for exhausting engine parts. In this work, molybdenum flame spraying is investigated to reduce the friction in, e.g., valvetrain parts. Pin on disc friction test was carried out with rotating speed of 150 mm/s, 30 N load, 7,000 m distance, and SUJ2 (100Cr6) pin at room temperature. As a result, after spraying with roughness Ra of 0.998 μm and after polishing Ra of 0.513 μm, friction coefficient in oil (GF4) was only 0.05, despite the fact that under dry sliding condition, it was 0.615 (Table 2.3). Mo sprayed and polished surfaces have high roughness (Ra 0.5–0.6 μm vs. PVD DLC 0.04 μm), but during sliding, the pores present in the coating act as oil reservoirs under oil-lubricated conditions, so the friction coefficient is comparable to that of DLC coating. Friction coefficient curve of thermally sprayed Mo coating is displayed in Fig. 2.10 and compared to that of DLC. It is shown that Mo spraying can be applied for valvetrain parts, except the material of counterparts is a powder metal. It is suitable for carbon-, Cr-, CrMo-containing steels as counterpart material regarding friction.

Furthermore, 8 wt.% yttria-stabilized zirconia (YSZ) was sprayed on turbine housing and exhaust manifold to reduce the heat effect to neighboring parts and to avoid the temperature reduction of exhaust gas that can reduce the amount of very expensive DPF catalytic material (Fig. 2.11). For heavy duty loaded big diesel engine, YSZ coating could protect the neighboring parts from heat effect, e.g., 30 % and increase in the temperature of exhaust gas.

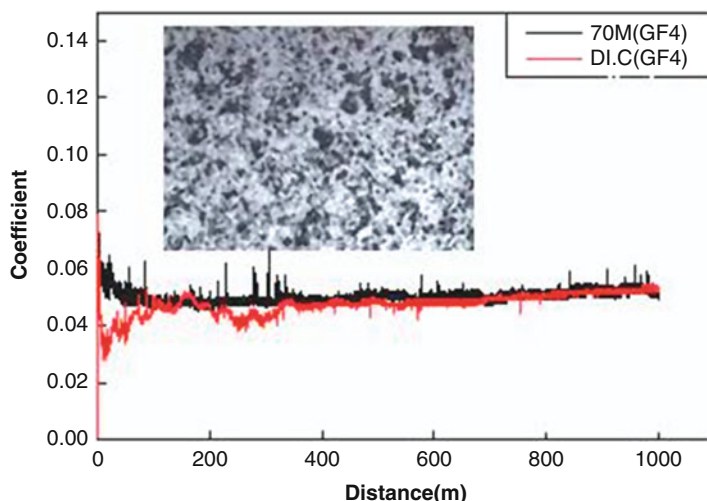


Fig. 2.10 Friction coefficient curve of Mo spray coating as a function of distance (compared with DLC's friction)



Fig. 2.11 YSZ sprayed exhaust parts

As a complementary technique for low friction to coating technology is surface texturing [8]. The idea is to make micro- or nano-sized dimples or grooves on surfaces, so oil for lubrication is trapped and the dimples play as an oil reservoir (Fig. 2.12). This effect can be better explained by Stribeck curve [9]. With the presence of shallow dimples, the curve shifts to left and down, i.e., the zone of elasto-hydrodynamic lubrication is enlarged. It is reported that application of this technique to all moving parts can lead to fuel economy improvement of 2 %. In addition, cylinder oil usage can be reduced by more than 15 %. Each part can be optimized with special pattern and dimple forms, sizes, and gaps to further optimize the lubrication performance.

In the near future, nano-sized particles with hybrid coating process can be realized. Many experts are now spending effort to develop high ionization efficiency and high-speed coating techniques. From the material view, multielements,

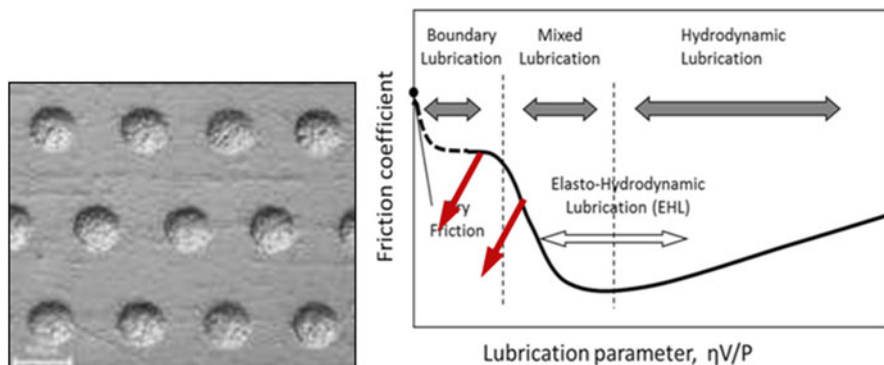


Fig. 2.12 Advanced coatings for automotive application [8, 9]

e.g., hard elements for hardness and soft elements for lubrication, can be mixed as amorphous phase to maximize the functionalities. Hybrid deposition machines enable, e.g., etching and buffer layer coating with high speed through arc process to enhance strong surface activation and adhesion and top layer by sputtering to have low roughness and droplets. High ionization and high-speed coating techniques can be realized by HIPIMS, ICP, and hollow cathode to increase the target usage rate. Not to mention, large area coating techniques having high speeds of over 20 m/min as well as surface treatment enable multiple functions on sheet metals, e.g., color change, self-cleaning, self-healing, and anti-dusting surfaces. In addition, fuel efficiency can be increased by creation of small-sized dimples on car body surfaces to reduce air resistance.

2.5 Conclusions

Low friction and wear resistant coatings, DLC, Si(O)-DLC, TiAlCrSiCN, nanodiamond PTFE coatings are applied for engine and transmission and high-temperature parts. Furthermore, Mo-sprayed coating for low friction and YSZ coating for heat protection are explained. Advanced coating techniques focus on high ionization, high-speed, hybrid, and large area coatings.

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Chapter 3

Overview of DLC-Coated Engine Components

Makoto Kano

Abstract Fuel-saving technologies have become more important in recent years, especially for automobiles, in order to avoid global environmental destruction and global resource depletion. In addition, the use of toxic elements such as phosphorus, sulfur, and chlorine in industrial lubricants must be decreased or eliminated. Technologies for reducing friction with environmentally friendly materials are direct ways of addressing environmental problems. Diamond-like carbon (DLC) coatings are increasingly being applied to the sliding parts of automotive engines, among other applications, to reduce friction and wear. These coatings have several advantages, including their harmless nature to the human body because they consist mainly of carbon, low friction, high wear resistance, and strong corrosion resistance.

This chapter discusses recent topics concerning the application of DLC coatings to automotive engine components. DLC coatings have already been successfully applied to the valve lifters and piston rings of mass-produced gasoline engines. The resultant effect on reducing friction in each application is described briefly. The effect of engine oil additives on the friction and wear properties of DLC coatings is also explained. Promising technologies for applying DLC coatings to future engine components are then presented.

The first topic discussed in this regard is the application of DLC coatings to aluminum alloys with sufficiently strong adhesion for obtaining high wear resistance. This can be accomplished by shot peening the aluminum alloy substrate with fine tungsten particles. A DLC coating deposited on A2017 and A5052 aluminum alloys (Japanese Industrial Standards) with this new process showed 40–80 % higher wear resistance and adhesion strength than DLC coatings formed by conventional processes. As a result, a DLC-coated aluminum alloy piston displayed superior wear resistance compared with that of a noncoated piston in a short-term engine firing test.

The second topic concerns super-low friction properties obtained by combining a DLC coating with an environmentally friendly lubricant. A super-low friction coefficient below 0.01 was obtained with a self-mated ta-C (tetrahedral amorphous carbon) coating lubricated with oleic acid, whereas an a-C:H (amorphous hydrogenated carbon) coating and bearing steel (JIS-SUJ2) did not display such a large

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reduction in the friction coefficient. This result implies that automotive engine fuel economy can be improved markedly by using completely environmentally friendly materials. These advanced technical results indicate that expanding the application of DLC coatings to various automotive components and mechanical parts used in other industries would be a promising approach for addressing global environment problems.

Keywords Diamond-like carbon (DLC) • Coating • Automotive engine component • Valve lifter • Piston ring • Fuel-saving • Reducing friction • Gasoline engine • Aluminum alloy • Super-low friction • ta-C • Tetrahedral amorphous carbon • a-C:H • Amorphous hydrogenated carbon

3.1 Introduction

In a technical paper entitled “Near-frictionless carbon coatings for use in fuel injectors and pump systems operating with low-sulfur diesel fuels,” it was reported that hydrogenated amorphous diamond-like carbon (DLC) coatings showed a super-low friction coefficient below 0.01 in sliding tests conducted in an inert atmosphere such as that of dry nitrogen gas [1–5]. That new finding about the superior friction property of DLC coatings triggered their accelerated application to automotive engine components for reducing friction. Since then, DLC coatings have been increasingly applied to the sliding interfaces of automotive components, such as valve lifters, piston rings, and fuel injectors, to improve wear resistance and reduce friction.

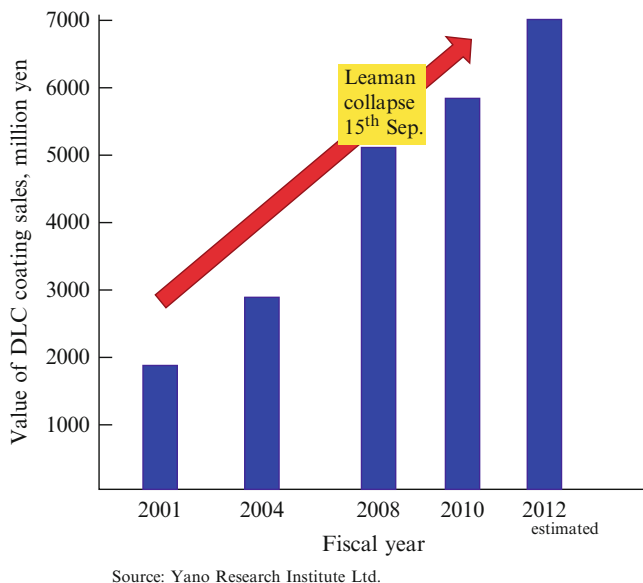


Fig. 3.1 DLC coating sales of Japanese coating producers

These applications to production engine components have consistently increased the sales of DLC coatings in Japan, as shown in Fig. 3.1. The total value of sales increased linearly from two billion yen in 2001 to seven billion yen in 2012, even though the world economy was drastically affected by the collapse of Lehman Brothers on 15th September 2008. The application of DLC coatings in the automotive industry has increased significantly both in terms of production volume and the kinds of applications involved.

The first part of this chapter describes the several successful applications of DLC coatings to automotive sliding components. These include the coupling clutch for torque control on 4-wheel-drive sport-utility vehicles (4WD SUVs), the differential gear on SUVs, the front fork on motorcycles, fuel injectors for automotive engines, piston rings for motorcycle and automotive engines, and valve lifters of automotive engines. The friction properties of DLC coatings are then explained based on the evaluations of engine components. Although the successful application of DLC coatings to mass-produced engine components has been expanding steadily, current applications are still far from fully using the excellent properties of DLC coatings. In this regard, there are several technical issues to be resolved, such as the technology for depositing DLC coatings on aluminum alloys with sufficient adhesion strength, optimum material combinations for reducing friction, and elucidation of the fundamental mechanisms of super-low friction.

The second part reviews recent technical topics concerning these issues. The first recent topic is an advanced technique for depositing DLC coatings on aluminum alloys with high adhesion strength for improving wear resistance. The targets of this application are gasoline engine pistons and cylinders. The main technical processes involved and the performance achieved to date are described.

There have been strong needs in recent years to find optimum material combinations for reducing mechanical friction, especially in automotive engines to improve fuel economy markedly. Reducing friction between cams and followers is effective in this regard in the low engine speed range. A DLC-coated valve lifter of the bucket type has been applied to gasoline engines to reduce engine friction substantially [6]. An ultra-low friction property has been obtained with a hydrogen-free DLC (ta-C) coating lubricated with engine oil containing glycerol mono-oleate (GMO) [7, 8].

Woydt has projected that polyalkylene glycol (PAG), which has the same hydroxide functional group as GMO, will be applied as an environmentally friendly automotive engine oil in the coming years [9, 10]. Therefore, the combination of a ta-C coating and PAG oil as an optimum pair of environmentally friendly materials can be expected to improve fuel economy by reducing engine friction. As one step toward that goal, the second topic concerns an evaluation of the potentiality for obtaining super-low friction properties with self-mated DLC/DLC contacts lubricated with an environmentally friendly fluid. A super-low friction coefficient below 0.01 was obtained with a self-mated ta-C coating, deposited by a filtered arc deposition process and lubricated with oleic acid.

With regard to future possibilities, it is forecast that friction losses in passenger cars could be reduced by 61 % in the long term (15–25 years) by taking advantage of new technologies [11]. DLC coating technology is one of the most promising approaches for achieving this formidable goal. In addition, material technology using a DLC coating combined with an environmentally friendly lubricant has great potential for addressing environmental problems in various industries.

3.2 DLC Coatings for Automotive Engines

3.2.1 Application to Engine Components

Typical examples of automotive components coated with DLC coatings in Japan are shown in Table 3.1. In this last decade, applications have increased markedly both in terms of production volume and variety. First, we will look at some applications other than engine components. For the coupling clutch application, an amorphous Si-doped hydrogenated carbon (a-C:H:Si) coating was applied to the steel plate that slides against the friction plate in the torque control system used on 4WD SUVs. The high wear resistance and high friction coefficient of the a-C:H:Si coating resulted in a compact clutch system. In addition, the fact that the friction coefficient of this coating has a positive slope relative to increasing sliding velocity provides higher shudder resistance [12].

For the SUV differential gear application, a tungsten carbide combined amorphous hydrocarbon (WC/a-C:H) coating was applied to the gear teeth to improve wear resistance. DLC coatings can increase the life of gears by suppressing scuffing wear or spalling wear. In gear applications, it is easy to coat a DLC film directly on the gear teeth as a measure for improving wear resistance because the film is very thin, around 1 μm in thickness, and the temperature in the coating process is very low, below 473 K, which means no additional surface finishing is needed.

For the application to the front fork of motorcycles, an amorphous hydrogenated carbon (a-C:H) coating was applied to the steel inner tube of the fork to reduce friction. This friction reduction helps to give the rider an excellent driving feel. This coating technology has also been applied to the sliding members of the suspension system on luxury vehicles [13].

Next, we will look at several applications to engine components. For the fuel injection systems of automotive engines, DLC coatings have been applied to several

Table 3.1 Applications of DLC coatings to automotive parts

Parts	DLC	Coating	DLC properties
SUV 4WD torque controlled coupling clutch	a-C:H-Si	PECVD	Excellent friction property and wear resistance
SUV differential gear	WC/a-C:H	PECVD	High wear resistance for extending gear life
Motor bike front fork, luxury vehicle suspension	a-C:H	PECVD	Excellent driving feel and high wear resistance
Fuel injector, pump	a-C:H	PECVD	High wear resistance in fuel at boundary lubrication
Motorcycle engine piston ring	WC/a-C:H	PECVD	High wear resistance mating with aluminum alloy of cylinder
Automotive engine valve lifters	ta-C	PVD	Ultra-low friction and high wear resistance
Automotive engine piston rings	ta-C	PVD	Ultra-low friction and high wear resistance

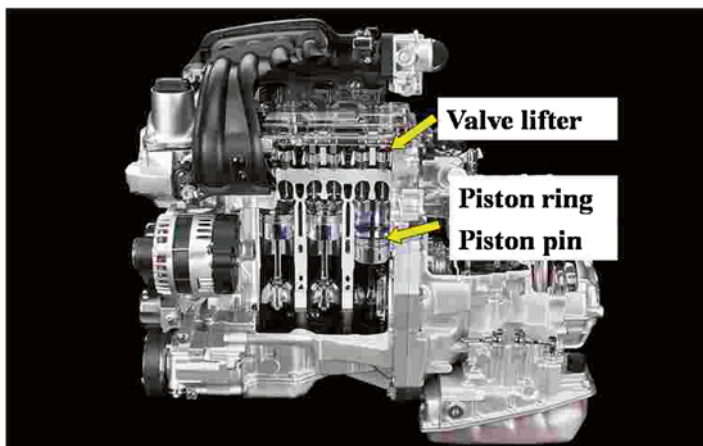


Fig. 3.2 ta-C coated components of a gasoline engine

components such as the plunger of high-pressure diesel fuel pumps. Because the sliding conditions of the fuel injector and other pump sliding parts have become severer due to higher contact pressure, several types of DLC coatings were evaluated for the purpose of obtaining higher wear resistance under boundary lubrication in the fuel [14].

The engine valve lifter is the most successful application of DLC coatings to a mass-produced component because a fuel-saving effect is clearly obtained by reducing friction. The shape of the valve lifter is adjusted to obtain stable coating quality because the lifter surface to be coated is flat. A tetrahedral amorphous carbon (ta-C) coating, desposited by an arc ion plating physical vapor deposition (PVD) method, has been applied to the valve lifters and piston rings of mass-produced gasoline engines to improve fuel economy as shown in Fig. 3.2. The friction properties were evaluated in motoring tests of an actual engine cam follower system [6, 8].

Engine bench tests using a production engine and a standard engine oil without any molybdenum dithiocarbamate (MoDTC) additive were conducted to examine the effect of the ta-C coating on reducing energy loss due to friction. The cylinder head was mounted on a test stand, and the camshaft made of chilled cast iron was driven directly by a drive motor via a torque meter, as shown in Fig. 3.3. Figure 3.4 shows the effect of various coatings on valve-train friction torque as a function of engine speed. The ta-C coating reduced friction torque by 45 % compared with the result for a conventional phosphate coating on carburized steel at an engine speed of 2,000 rpm. On the other hand, the effect of the a-C:H coating on reducing friction was lower than that of the ta-C coating and comparable to that of titanium nitride (TiN). A durability test was then conducted at an engine speed of 4,000 rpm for about 300 h, and none of the cam follower interfaces tested showed any adhesive or abrasive wear or noticeable peeling of the coating. These results confirmed the superior wear resistance of ta-C coated valve lifters. From autumn of 2006, ta-C

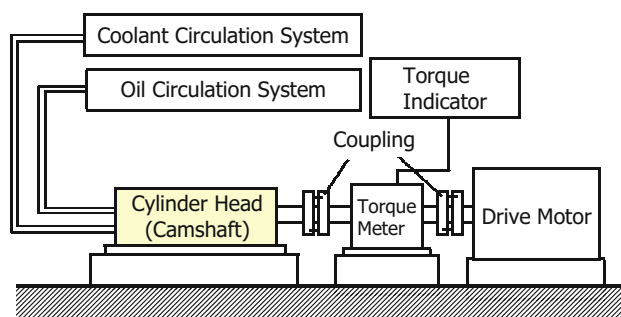


Fig. 3.3 Automotive engine motoring test method

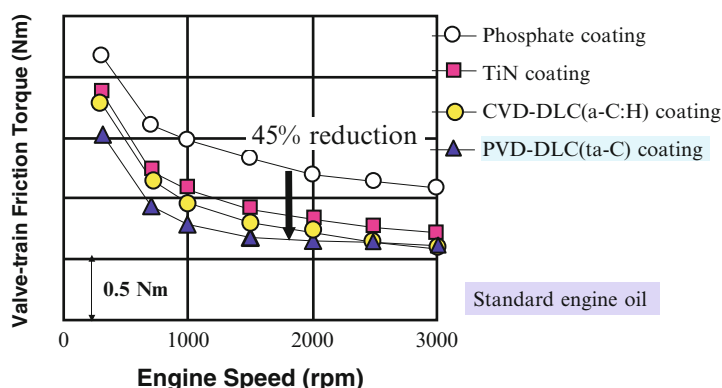
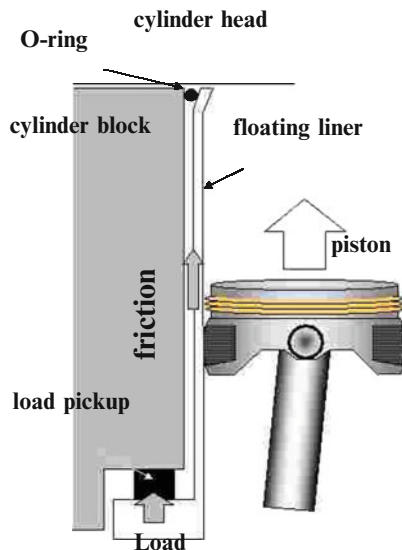


Fig. 3.4 Friction reduction obtained with different coatings

coated valve lifters have been used in a mass-produced V6 gasoline engine together with a new gasoline engine oil containing GMO. This new material technology has reduced fuel consumption by about 2 %.

This ta-C coating has been applied recently to both the compression ring and the oil ring of a new mass-produced inline three-cylinder compact gasoline engine. Friction force, indicated as the distance between the positive and negative values, was evaluated in an engine firing test using a single-cylinder gasoline engine lubricated with a standard gasoline engine oil, as shown in Fig. 3.5 [15]. It was found that a large friction reduction was obtained for the ta-C coated compression and oil rings at different crank angles, specifically around 0° for the compression ring and over a wide range of angles of 180 , 360 , -180 , and -360° , but excluding 0° , for the oil ring, as shown in Fig. 3.6. These results suggested that a severe boundary lubrication condition probably formed at these different crank angles for the compression and oil rings. It would be too difficult to measure these different friction properties directly at the sliding interfaces between the piston rings and the cylinder wall during actual engine operation.

Fig. 3.5 Friction measurement using a single-cylinder test engine



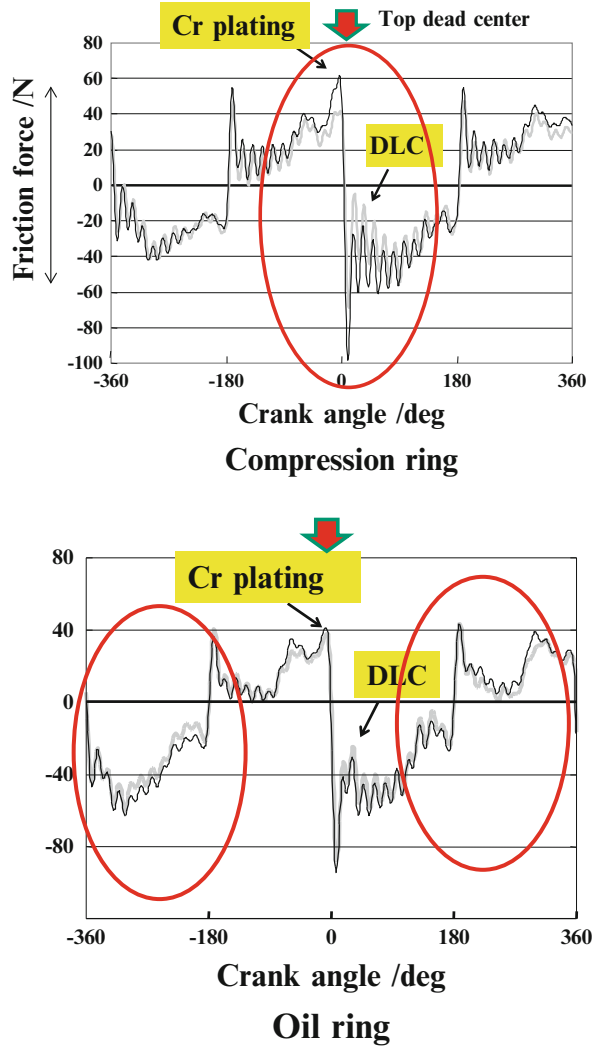
Besides hardened steel, two other applications of DLC coatings on lightweight metals have been reported. These applications were for a lightweight valve lifter made of a beta titanium alloy and a valve spring retainer made of an aluminum alloy. A DLC coating was used to increase wear resistance substantially [16, 17]. As another example of an engine component application, a DLC coating was applied to the slider pad of a switching roller finger follower to make the pad more compact [18]. In these applications, the reduction of both weight and friction had the effect of improving vehicle fuel economy. In the near future, it is forecast that DLC coatings will be applied to many kinds of engine sliding components made of lightweight materials, thereby greatly expanding the range of coating application.

3.2.2 Effect of Lubricant on Friction and Wear Properties of DLC Coatings

Since all sliding engine components are usually lubricated with engine oil, it is very important to investigate the friction properties of DLC coatings under a lubricated condition. This section describes the effect of lubricants on the friction and wear properties of DLC coatings.

The super-low friction property of DLC coatings is affected by the operating environment conditions, as mentioned earlier. Therefore, it has been very important to evaluate the friction properties of DLC coatings under a lubricated condition to find the right additives for substantially reducing friction. Because automotive engine oil contains many kinds of complex additives such as zinc dialkyl dithiophosphate

Fig. 3.6 Friction force measured for Cr-plated and ta-C coated piston rings



(ZDDP), it was difficult to identify clearly the interactions between the additives and DLC coatings [19–24]. Pin-on-disc sliding tests were conducted to evaluate the effect of one simple modifier on the friction properties of DLC coatings. Typical DLC coatings selected for evaluation in this way included hydrogenated amorphous carbon (a-C:H) and hydrogen-free tetrahedral amorphous carbon (ta-C). Sliding tests were conducted at high Hertzian pressure of 700 Mpa under oil lubrication at a temperature of 353 K. The effect of various friction modifier additives on the friction properties of these DLC coatings was evaluated when used with a poly-alpha-olefin (PAO)-based oil. Many types of friction modifier additives were examined, including amine, amide, and ester (GMO). It was found that a ta-C

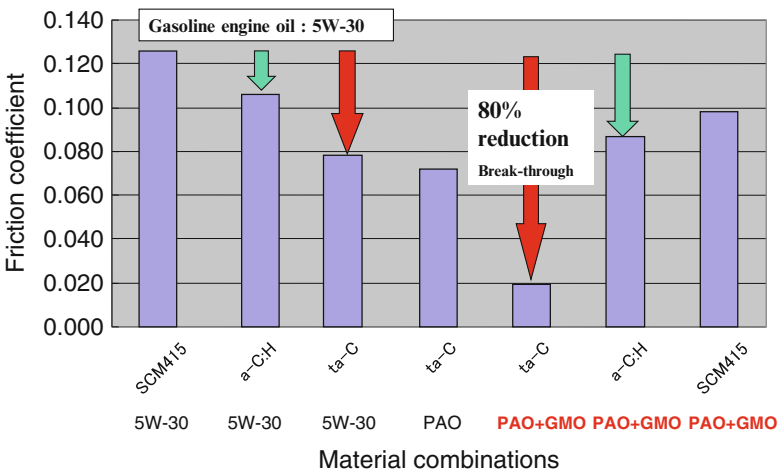


Fig. 3.7 Ultra-low friction property of ta-C under GMO-containing oil lubrication

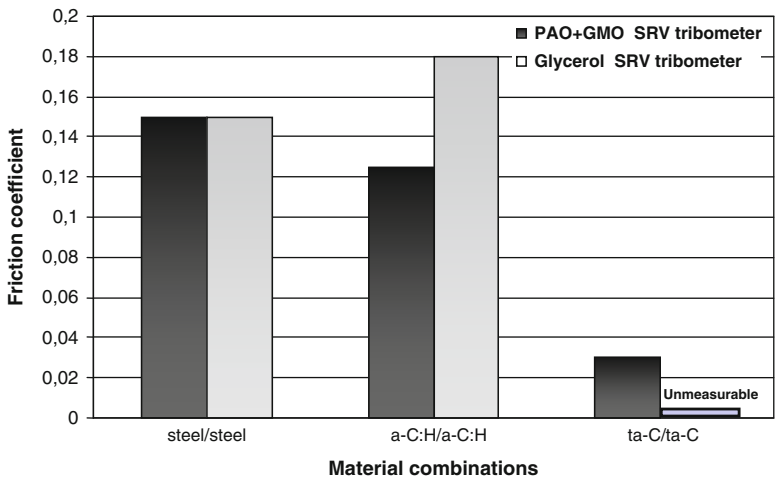


Fig. 3.8 Super-low friction of self-mated ta-C under glycerol lubrication

coating/steel pair lubricated with a PAO oil containing 1 mass % of ester (PAO+GMO) showed an ultra-low friction coefficient of 0.02, whereas an a-C:H coating/steel pair displayed a much higher friction coefficient of 0.09 and that of a steel/steel pair was 0.100, as shown in Fig. 3.7 [25].

Friction properties of DLC coating pairs lubricated with PAO+GMO at a temperature of 353 K were also evaluated in SRV tests to make clear the reason for ultra-low friction. Figure 3.8 shows the friction coefficients obtained for different kinds of material combinations lubricated with PAO+GMO and pure glycerin. Amazing results were obtained for the ta-C/ta-C coating combination. The friction coefficients

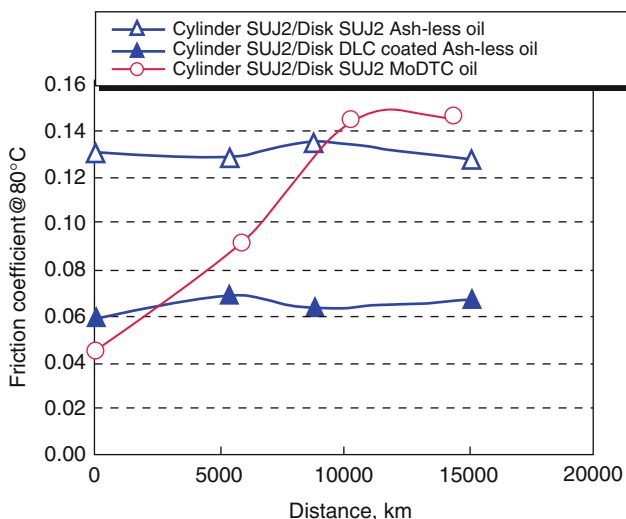
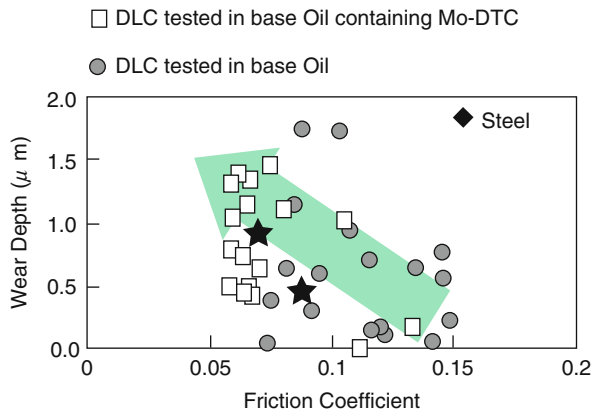


Fig. 3.9 SRV friction test results for different oils following driving tests

of the ta-C pairs were substantially lower than those of the a-C:H ones. These results strongly suggest that ultra-low friction was obtained by the interaction between the ta-C coating and the ester-containing oil; this property is attributable to the formation of a very thin, low-shear-strength tribofilm on the ta-C sliding surface, and a better lubrication condition. Moreover, super-low friction and zero-wear behavior was notably obtained for the ta-C/ta-C coating combination lubricated with pure glycerin at 80 °C. As shown in Fig. 3.8, the friction coefficient was below 0.01 and was actually not measurable with the equipment used. Moreover, the wear scar was not visible when viewed under an optical microscope. This result suggests that superlubricity is related to an alcohol chemical function (OH), which is common to both GMO and glycerol molecules. Test results for the interaction between the ta-C coating and GMO that resulted in an amazing reduction of friction are described below.

The friction coefficients obtained for a ta-C coating and bearing steel (JIS-SUJ2) in SRV tests using two kinds of engine oil at different driving distances are shown in Fig. 3.9 [26]. The results indicate that the very low friction property of the ta-C coating in ester (GMO)-containing engine oil was maintained even after 5,000 km, whereas the friction coefficient of the steel specimens in the MoDTC-containing engine oil increased markedly after 5,000 km. The latter result implies that the solid lubricant film (MoS₂) that formed on the steel sliding surface from MoDTC was consumed as the distance increased. This suggests that some other mechanism than the formation of a solid lubricant film was the reason why a low friction coefficient was maintained for a longer distance. Judging from these results, the friction properties of DLC coatings are affected by the kind of lubricant used. The following discussion concerns the effect of engine oil additives on the wear properties of DLC coatings.

Fig. 3.10 DLC coating wear acceleration by MoDTC-containing engine oil



3.3.1 Method of Applying DLC Coatings to Aluminum Alloys

3.3.1.1 Fundamental Tests of Experimental Coating Methods

Two kinds of aluminum alloys, 2017 and 5052, specified in the AISI standards were used for the substrates that received the DLC coating. Disc samples measuring 33 mm in diameter and 3 mm in thickness were coated. A smooth disc surface with an average surface roughness R_a of less than $0.05\text{ }\mu\text{m}$ was obtained by polishing. The surface was hardened by shot peening using fine tungsten particles smaller than $53\text{ }\mu\text{m}$ in size as shown in Fig. 3.11. The particles were projected on the disc surface at a speed higher than 50 m/s for 5 s. The sharp top edges formed on the surface during the shot-peening process were subsequently removed by light polishing. The a-C:H coating was then deposited on the aluminum substrates to a thickness of about $1\text{ }\mu\text{m}$ by plasma chemical vapor deposition (PCVD). It proved to be too difficult to coat the ta-C film on the rough disc surface with sufficient adhesion strength after the surface hardening treatment. Therefore, the a-C:H film was used for the DLC coating on the aluminum piston and cylinder.

The adhesion strength and wear resistance of the DLC film coated on the aluminum substrates were evaluated in sliding tests under a continuously increasing load [31, 32]. The tests were conducted with a ball-on-disc sliding tester as shown in Fig. 3.12. The ball material was an alumina ceramic with high hardness comparable to that of the DLC coating. In accordance, compared with hardened steel such as AISI 52100, the initial contact pressure did not decrease appreciably owing to the suppression of large wear. The size of the ball was 3/8 in. in diameter. The sliding speed was 0.1 m/s and the load was increased at a rate of 5 N/min. The friction coefficient and acoustic emission (AE) were measured simultaneously.

The critical load, which was defined as the applied load where the friction coefficient increased markedly, was evaluated as an index of the adhesion strength and wear resistance of the DLC coating. The optimum conditions of the shot-peening

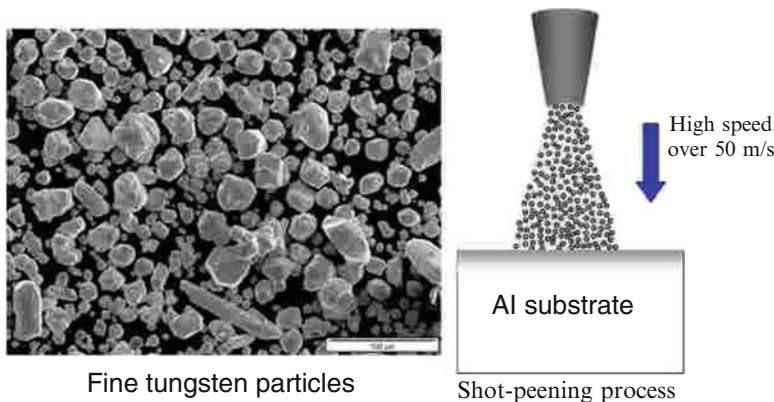


Fig. 3.11 Fine tungsten particles used in the shot-peening process

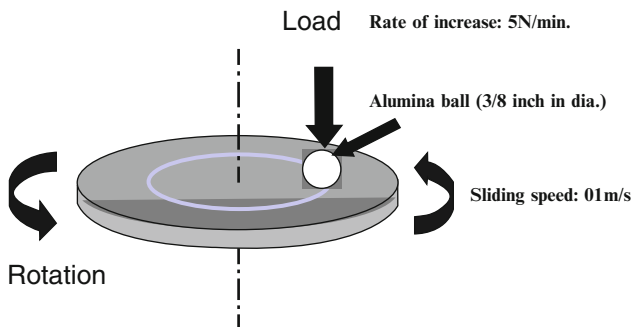


Fig. 3.12 Sliding test under continuously increasing load

process were selected in reference to this critical load. Finally, the excellent wear resistance of DLC-coated aluminum alloy pistons and cylinders was confirmed in tests conducted with actual motorcycle engines.

3.3.1.2 Results and Discussion

The surface of the aluminum alloy substrates was modified by the shot-peening process using fine tungsten particles. Cross-sections of the A5052 alloy are shown in Fig. 3.13. The upper photo is a backscattered electron composition image in which the white-colored part corresponds to the heavy element tungsten. The X-ray images of the aluminum and tungsten elements in the figure indicate that a dispersed layer of fine tungsten particles formed near the top surface with a thickness of about 10 μm . This dispersed layer was probably formed by the mixing of the destroyed tungsten particles and aluminum due to plastic deformation. The dispersed tungsten layer was also formed near the top surface of the A2017 alloy.

The micro-hardness numbers near the top surface of these cross-sections were about 20–30 % higher than those of the substrate and decreased steadily from the surface to the substrate, as shown in Fig. 3.14. The hardened layers were about 40–50 μm in thickness and consisted of the dispersed tungsten particle layer on the mechanically hardened layer.

The thick hardened layer obtained by shot peening displayed much larger surface roughness and there were many sharp peaks on the surface. When the DLC film was coated on the substrate right after the shot-peening process, abnormally thick deposits were found around the sharp peaks, as shown in Fig. 3.15. Therefore, the sharp peaks were removed by light polishing before the coating process. As a result, a uniform DLC film was formed on the modified substrates. The surface roughness of the DLC film obtained after lightly polishing the sharp peaks had a plateau shape, as shown in Fig. 3.16.

The adhesion strength and wear resistance of the DLC coating on the aluminum alloy substrates were evaluated in sliding tests with a continuously increasing load.

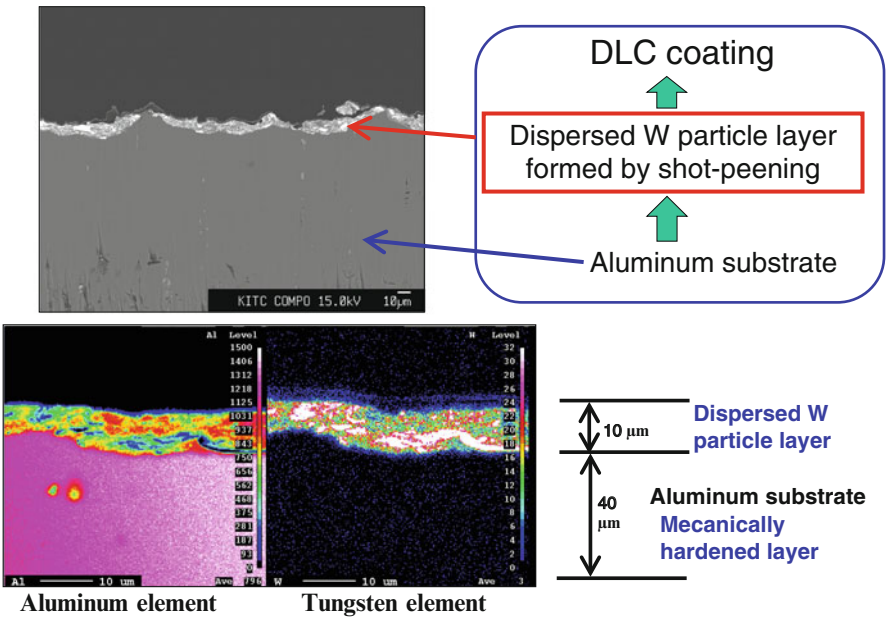


Fig. 3.13 Dispersed tungsten layer by shot-peening

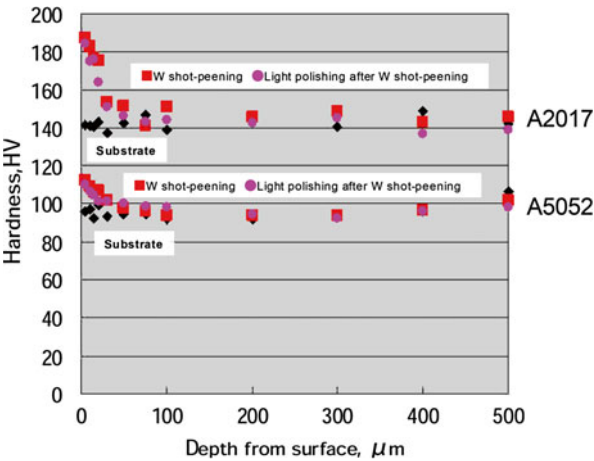


Fig. 3.14 Higher hardness obtained by shot-peening process

For the polished A5052 substrate, the AE signal initially showed a pronounced increase, followed soon by an increasing friction coefficient around a 40-N load, as shown in Fig. 3.17. These results suggest that the DLC coating fractured partially and then the friction coefficient increased due to direct contact with the aluminum substrate. The load where the friction coefficient increased markedly over 0.5 was

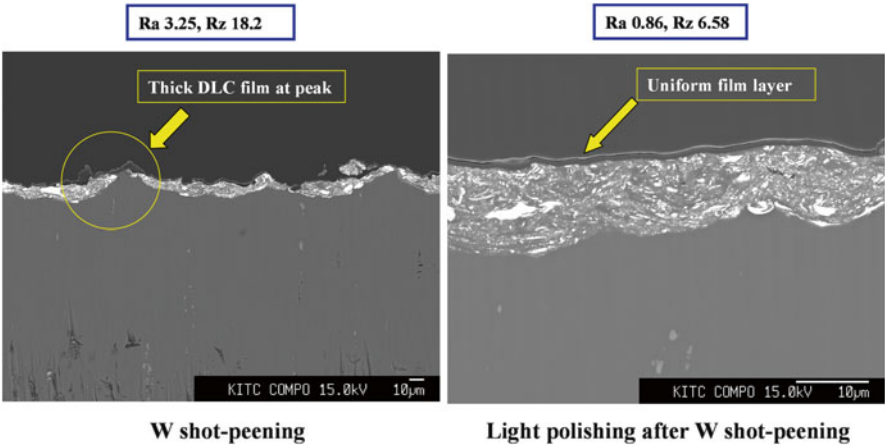
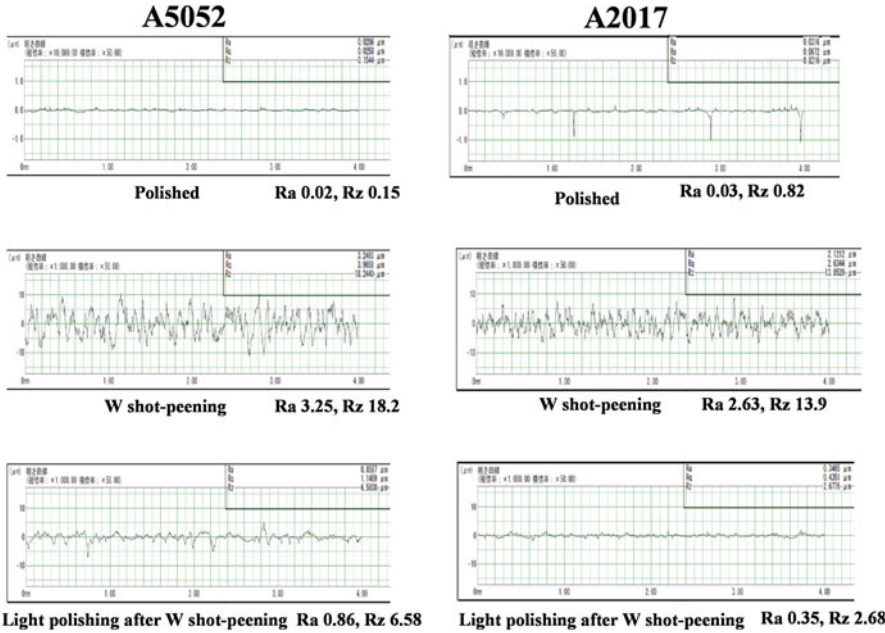


Fig. 3.15 Comparison of DLC coatings on modified Al substrate



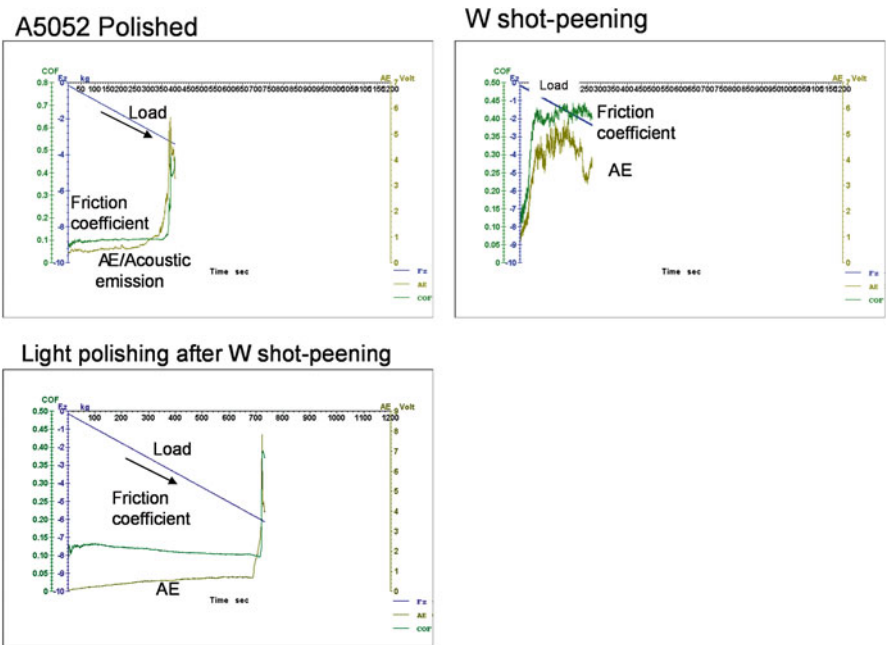


Fig. 3.17 Friction coefficient and AE signal of DLC coatings on A5052

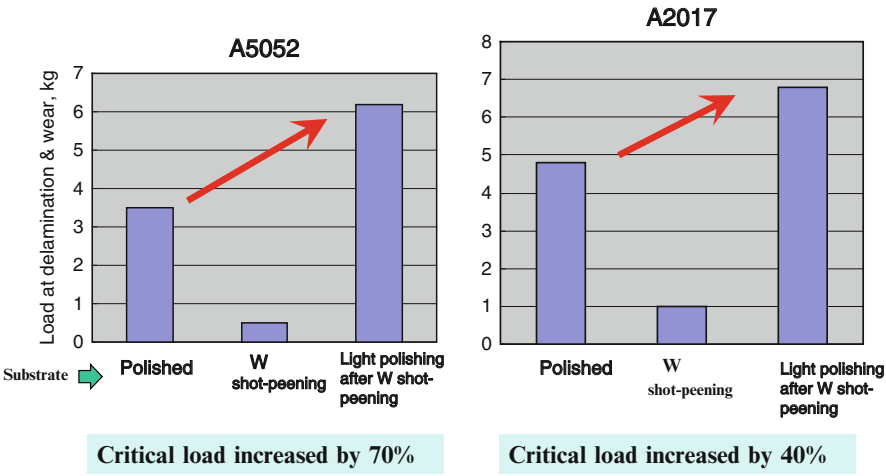


Fig. 3.18 Critical load of DLC coatings on A5052 and A2017

pressure and that heavy adhesive wear occurred between the alumina ball and the aluminum substrate. In contrast, the critical load of the DLC coating on the substrate that was polished lightly after shot peening was much higher than that of the coating on the polished substrate.

High wear resistance of DLC-coated Al piston



Engine spec.: 125 cc single-cylinder, 4-cycle, air cooled

Engine test : Eng.speed 1000~13000rpm for 10minutes



A2618 Heat-resistant Al alloy
Cylinder bore : Ni-P plating



A2618⇒DLC coating applied after W shot-peening and light polishing
Cylinder bore : PCVD DLC

Fig. 3.19 DLC-coated aluminum alloy piston

The critical load of the DLC coating on the A2017 substrate showed the same tendency, as shown in Fig. 3.18. The critical load was clearly higher than that of the coating on A5052 for each substrate specification. This result suggests that the DLC coating on the substrate with higher hardness displayed a higher critical load, based on a comparison of Figs. 3.14 and 3.18. The substrate surface treatment probably produced a smaller increase in the critical load of the DLC coating on A2017 compared with that of the coating on A5052 due largely to the removal of the dispersed tungsten particle layer because the roughness of the coating on the former substrate was smaller than that of the coating on the latter substrate, as shown in Fig. 3.16. This result implies that the presence of dense tungsten particles was required to increase the critical load.

This original DLC coating technology has been applied to aluminum alloy pistons of motorcycles. An A2618 aluminum alloy with a low Si content was used for the pistons because the development concept was to reduce Si precipitates that are characterized by poor workability. Si precipitates also showed the formation of many cracks after the tungsten shot-peening process. Therefore, the critical load of DLC coatings on aluminum alloys containing a large amount of silicon did not show any improvement. Engine firing tests were conducted as shown in Fig. 3.19. The DLC (a-C:H:PCVD)-coated piston clearly showed better scuffing wear resistance than the noncoated piston.

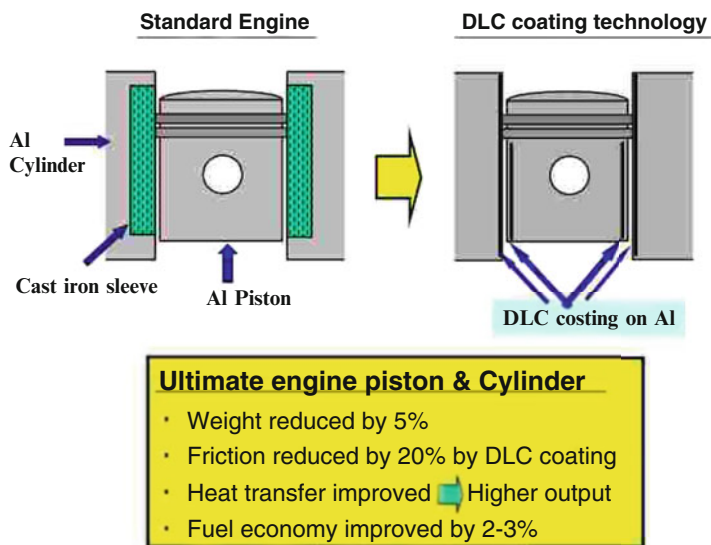


Fig. 3.20 Target of DLC-coated aluminum alloy piston and cylinder for ultra-low friction engine

DLC coated piston & cylinder after engine firing test

2000rpmx5min., 5000rpmx5min., 12000rpmx3min , Motorcycle gasoline engine oil 0W-20

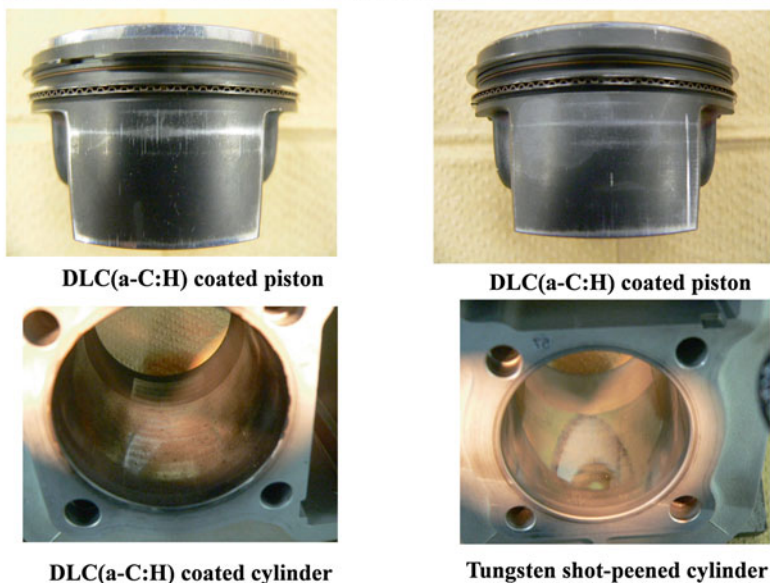


Fig. 3.21 Wear condition of DLC-coated piston and cylinder after engine firing test

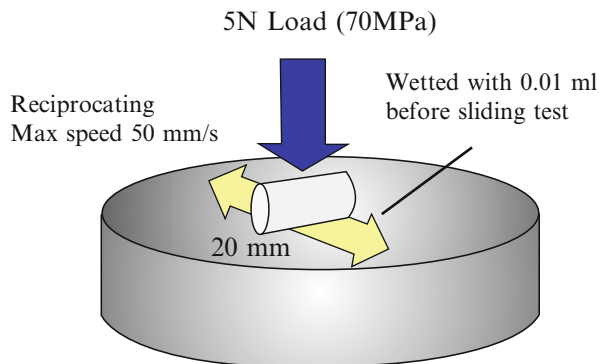
This DLC coating technology was then applied directly to aluminum engine cylinder walls to develop an ultra-high performance engine as shown in Fig. 3.20. After the shot-peening process was performed with very fine particles of 5 μm in diameter, the surface roughness did not become worse. Therefore, light polishing following the shot-peening process was not required and the a-C:H coating was deposited directly on the fine tungsten particle shot-peened AC4C cast aluminum alloy surface. Finally, an engine firing test was conducted to evaluate the wear resistance of the DLC-coated aluminum piston and cylinder. A tungsten shot-peened cylinder without a DLC coating was also evaluated with the DLC-coated aluminum piston. The wear condition of these pistons and cylinders is shown in Fig. 3.21. For the DLC coating pair, the coating on the piston wore off partially, although the sliding track on the cylinder seemed very smooth without any severe deep scuffing grooves. In contrast, the wear condition of the DLC-coated piston and tungsten shot-peened cylinder seemed much better than that of the DLC coating pair. The combination of the DLC-coated aluminum piston and the tungsten shot-peened cylinder is a promising technology for application to automotive gasoline engines to improve fuel economy substantially.

3.3.2 Super-Low Friction Obtained with DLC–DLC Pair Under Oleic Acid Lubrication

3.3.2.1 Experimental Method

Fundamental research on an optimum material combination of a DLC coating and a simple lubricant for reducing friction to an ultra-low level is presented here as a second topic [33–35]. Pin-on-disc reciprocating sliding tests were conducted in the following manner. The pins, measuring 9 mm in diameter and 9 mm in length, were made of hardened bearing steel (AISI 52100) and polished to a surface roughness below 0.05 μm . The disc, measuring 33 mm in diameter and 3 mm in thickness, was made of AISI 52100 and polished to a surface roughness below Ra 0.05 μm . Three kinds of DLC coatings were applied to the pins and discs: an a-C:H coating deposited by plasma enhanced CVD to a 1- μm thickness, a ta-C coating deposited by the arc ion PVD method to a 1- μm thickness, and a ta-C(T) coating deposited by the T-filtered arc PVD method [36] to a 0.3- μm thickness. Surface droplets in the ta-C coating were removed by slight polishing after the coating process. The specifications of the disc coating and surface roughness are shown in Table 3.2. The pin was secured to prevent it from rotating and was pressed against the reciprocating disc as shown in Fig. 3.22. Contact at the sliding interfaces was in the shape of a line under high Hertzian pressure of 70 MPa. The maximum sliding speed was 0.05 m/s and the stroke was 20 mm for the reciprocating test. Lubrication with oleic acid was provided by wetting the disc with several droplets (0.01 ml) at ambient temperature.

Fig. 3.22 Reciprocating sliding test setup



3.3.2.2 Results and Discussion

Friction curves with greatly different shapes were observed for sliding times from 0 to 30 min as shown in Fig. 3.23. The friction coefficient of the AISI 52100 steel pair (steel/steel) was at a very low level of 0.02 for 300 s and then increased gradually to a final level of 0.085. That of the a-C:H pair (a-C:H/a-C:H) decreased from 0.08 to 0.045 for 1,200 s and then stayed at a stable level. That of the ta-C pair (ta-C/ta-C) decreased continuously from a high level of 0.09–0.045. In contrast, that of the ta-C(T) pair (ta-C(T)/ta-C(T)) decreased from a very low level of 0.02 to a super-low friction regime below 0.01 in a very short time and stayed at a very low level of 0.015 for 1,800 s.

The steel pair showed an ultra-low friction coefficient initially, which was probably due to the tribochemical reaction with oleic acid. The friction coefficient then increased gradually above 0.08 due to increasing surface roughness caused by wear. For the DLC pairs, the ta-C pair showed a much larger friction coefficient reduction than the a-C:H pair. The higher friction coefficient especially in the initial period for the ta-C pair was presumably caused by the larger surface roughness due to the presence of many droplets compared with that of the ta-C(T) pair. Therefore, the effect of the ta-C pair on reducing friction was probably comparable to that of the ta-C(T) pair. Of course, the mechanism of the super-low friction properties of these DLC coatings must be made clear, but it will take a long time to obtain definitive evidence due to the difficulty of conducting surface analyses. It can be concluded that DLC coatings have an exceptionally high potential to provide super-low friction properties in combination with environmentally friendly fluids such as oleic acid lubrication.

Finally, the friction properties of DLC–DLC coating combinations for engine pistons and cylinders were evaluated in reciprocating sliding tests at ambient temperature under a condition of gasoline engine oil lubrication containing GMO ester. The DLC coating on the AISI 52100 steel pin was only a-C:H to simulate the engine cylinder surface because the PCVD process can deposit this type of coating to a uniform thickness on the inner wall of the cylinder. A few types of DLC coating,

Table 3.2 Specifications of DLC coatings for discs

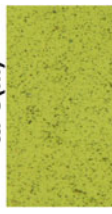
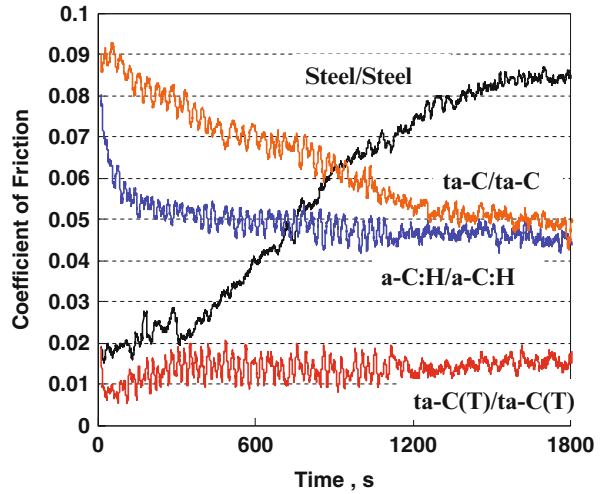
	No coating	a-C:H	ta-C(T)	ta-C
Coating method	Steel (SUJ2)	Plasma CVD	PVD (T-FAD)	PVD (normal)
Thickness, μm	—	1.1	0.3	0.9
Hardness, GPa	—	20	61	60
Ra, nm	3.1	3.6	4.5	15.6
	No coat  (μm) 測定範囲: ×10,000.00 解像率: ×50.00	a-C:H  (μm) 測定範囲: ×10,000.00 解像率: ×50.00	ta-C(T)  (μm) 測定範囲: ×10,000.00 解像率: ×50.00	ta-C(M)  (μm) 測定範囲: ×10,000.00 解像率: ×50.00

Fig. 3.23 Super-low friction property of ta-C(T) pair under oleic acid lubrication



Sliding conditions: Pin on disc, Reciprocating motion, Sliding length:10mm, Max. speed:10mm/s, Load:5N, Lub: Gasoline engine oil(GMO), 0.01ml drops

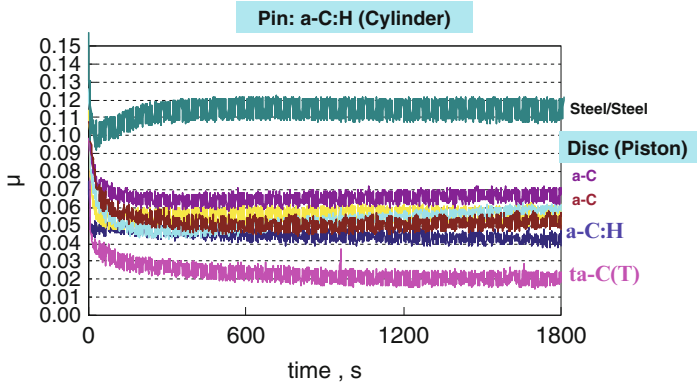


Fig. 3.24 Ultra-low friction of DLC–DLC coating combinations under engine oil lubrication

including the a-C type deposited by a sputtering PVD process, were applied to the AISI steel disc to simulate the engine piston skirt surface.

A large effect on reducing friction was confirmed for combinations of the a-C:H-coated pin with a few types of DLC-coated discs as shown in Fig. 3.24. The ta-C(T)-coated disc reduced friction by 80 % compared with that seen for the steel disc, although it is necessary to develop a way of applying this coating to aluminum alloys with high adhesion strength for obtaining wear resistance comparable to that of the a-C:H coating. Judging from these results, the use of these DLC-coated aluminum pistons and cylinders can be expected to reduce fuel consumption by a few percent.

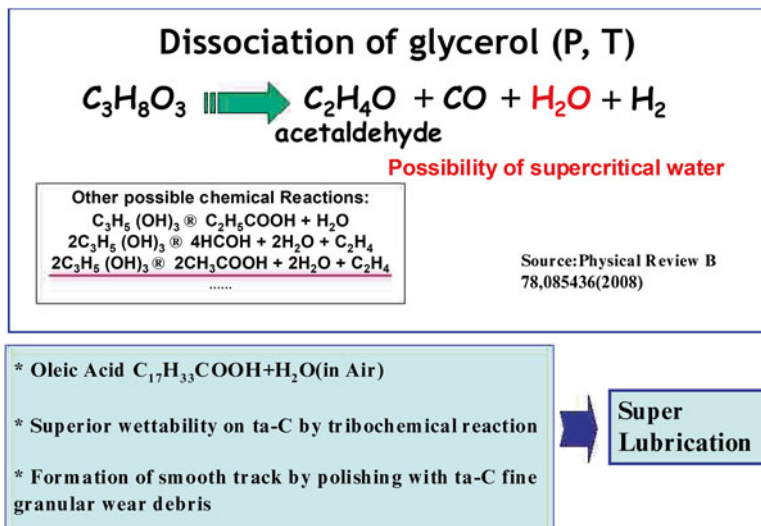


Fig. 3.25 Possible mechanism of ultra-low friction

Martin et al. proposed a possible mechanism for super-low friction whereby a water layer is formed by the tribochemical reaction between the ta-C coating and glycerol, among other elements [37, 38]. They indicated that the formation of water and acid might result from a chemical reaction with glycerol, as shown in Fig. 3.25. In the test using the oleic acid, water could be supplied from the ambient air. Therefore, the super-low friction obtained with the ta-C(T) coating lubricated with oleic acid might be attributable to the formation of a low-shear-strength tribofilm and excellent lubrication at the sliding interface. In addition, it was found that a very smooth surface was required to maintain the tribofilm. In accordance, super-low friction was probably obtained because of this superlubrication condition.

Although accurate and direct experimental data are needed to make clear this super-low friction mechanism, enhanced friction reduction effects are expected to be obtained in many industrial fields in the near future through the application of simple combinations of environmentally friendly materials, as shown in Fig. 3.26.

3.4 Conclusions

The application of DLC coatings to the sliding surfaces of automotive engine components has been increased successfully to improve wear resistance and reduce friction for valve lifters, piston rings, and fuel injectors, among other parts. In addition, promising technology has been developed for applying DLC coatings to aluminum alloys with high adhesion strength for obtaining better wear resistance. The critical load of the adhesion strength and wear resistance for a DLC (a-C:H) coating on an

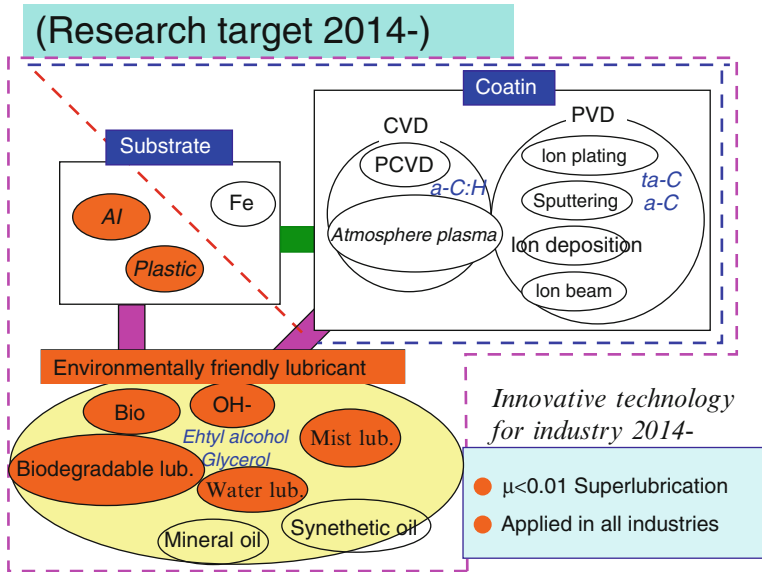


Fig. 3.26 Innovative DLC coating technology combined with lubricants for industrial applications

aluminum alloy substrate that was polished lightly after fine tungsten shot peening was much higher than that of a coating on a polished substrate. Another promising technology involves material combinations of a DLC coating and an environmentally friendly lubricant to obtain ultra-low friction. A ta-C/ta-C pair under oleic acid lubrication showed a marked friction reduction to a super-low friction level. These experimental results indicate that applying DLC coatings can be a very promising approach for addressing global environmental problems.

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Chapter 4

Coating Technologies for Automotive Engine Applications

Arup Gangopadhyay

Abstract Coatings are materials deposited on surfaces to enhance a specific set of performance attributes, i.e., wear resistance, erosion resistance, corrosion resistance, friction reduction, etc. Since wear, corrosion, and friction phenomenon are restricted on the surface, deposition of a coating provides a great flexibility in imparting properties which could be significantly different from the parent material. There are wide varieties of materials available for deposition and the choice of a material depends on the application, compatibility with the base material, and the deposition process. This chapter first reviewed lubrication regimes in critical tribological contacts (cam and tappet in valvetrain, piston and piston rings and cylinder bore, piston pins, and bearings) in an engine to justify where coatings could improve friction reduction and durability. Then, described coatings being used/explored in each of these applications followed by an outlook of coating technologies in future automotive engines.

Keywords Valvetrain • Piston skirt • Piston rings • Bearings • Piston pins • Diamond-like carbon coating • PTWA coating • Polymer coating

4.1 Introduction

Coatings are materials deposited on surfaces to enhance a specific set of performance attributes, i.e., wear resistance, erosion resistance, corrosion resistance, friction reduction, etc. Since wear, corrosion, and friction phenomenon are restricted on the surface, deposition of a coating provides a great flexibility in imparting properties which could be significantly different from the parent material. The coating material may have a very different chemical composition than the base material. Generally, ferrous-based

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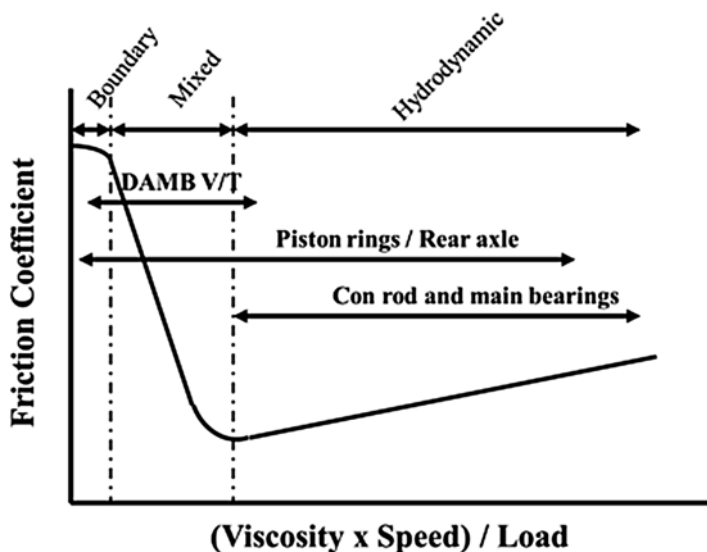


Fig. 4.1 Stribeck curve of engine systems

materials offer improved wear resistance compared to other engineering alloys. However, under extreme conditions, the wear resistance of ferrous material may need to be improved further through deposition of coatings. There are wide varieties of materials available for deposition, and the choice of a material depends on the application, compatibility with the base material, and the deposition process.

In order to understand the role of coatings in engine applications, it is important to understand the various lubrication regimes that exist during operation of an engine. For the sake of simplicity, it is better to focus on steady-state operations where the load and speed are held constant. Figure 4.1 shows a Stribeck curve where the operating regimes of various engine systems are superimposed. It can be observed that several of the systems operate in multiple lubrication regimes depending on speed. The valvetrain system, particularly the cam, and cam follower primarily operate in the boundary and mixed lubrication regime, whereas the bearings (main and connecting rod) operate primarily in hydrodynamic regime. The piston assembly system operates in all three regimes. In hydrodynamic lubrication regime, the asperities on the surface do not touch each other and are separated by a lubricant film; therefore, deposition of a coating on surfaces would not be effective in enhancing performances. However, in boundary and mixed lubrication regimes, the surface asperities touch each other, more so in boundary regime than on mixed regime, and therefore, opportunities lie in enhancing performances by deposition of a coating. The following section will address valvetrain system and power cylinder system separately.

4.2 Valvetrain System

There are five types of valvetrain systems as shown in Fig. 4.2. Type I valvetrain is the simplest where the lobes on the camshaft act directly on a bucket tappet, which could be either mechanical or hydraulic. In type II valvetrain, the lobes on the camshaft act against a roller. In type III and type IV valvetrain, the camshaft slides against a rocker pad. In type V valvetrain, the camshaft either slides or rolls against a follower. In modern engines, the vast majority of valvetrains are either type I or type II. Type II valvetrain offers lower friction because of rolling action but it is generally more expensive than type I and also makes engine taller because of packaging. This section will devote attention to type I valvetrain because there are opportunities for friction reduction through coatings.

Figure 4.3a shows a typical friction trend in a type I valvetrain as a function of camshaft speed. Basically this shows the left side of Stribeck curve indicating the operation in boundary and mixed lubrication regimes. Figure 4.3b shows Lambda ratio as a function of speed. If the typical surface roughness (R_q) of cam lobes and tappets after the surfaces are broken in is $0.04\text{ }\mu\text{m}$, then the composite surface roughness is $0.056\text{ }\mu\text{m}$, which translates into specific film thickness in the range $0.36\text{--}1.61$ confirming boundary and mixed lubrication regime operation. Nearly 85 % of the friction in this architecture [1] is at the cam and tappet contact and the rest are in cam bearings and valve guides. Therefore, attention should be paid at the cam follower contact. Since tappets are much smaller in size compared to camshafts, it is more economical to deposit coating on tappets.

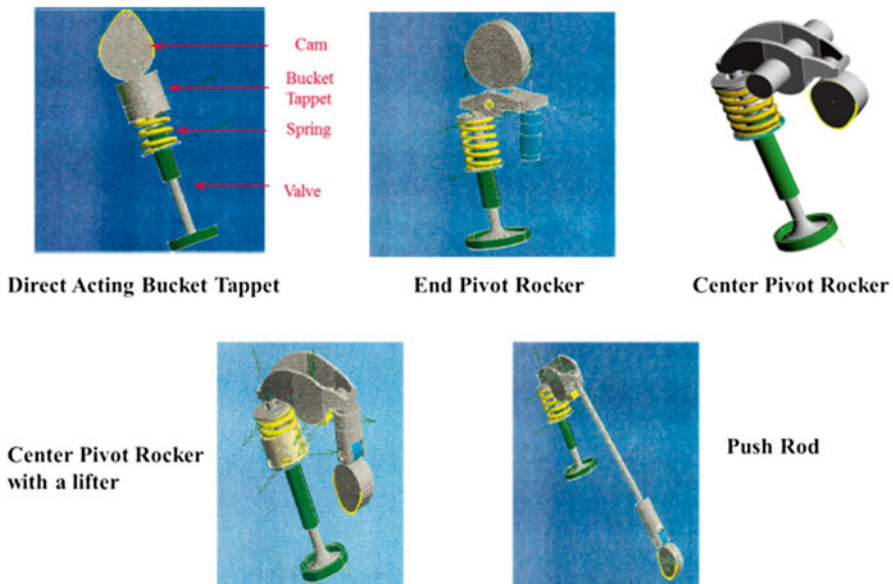


Fig. 4.2 Five types of valvetrain system

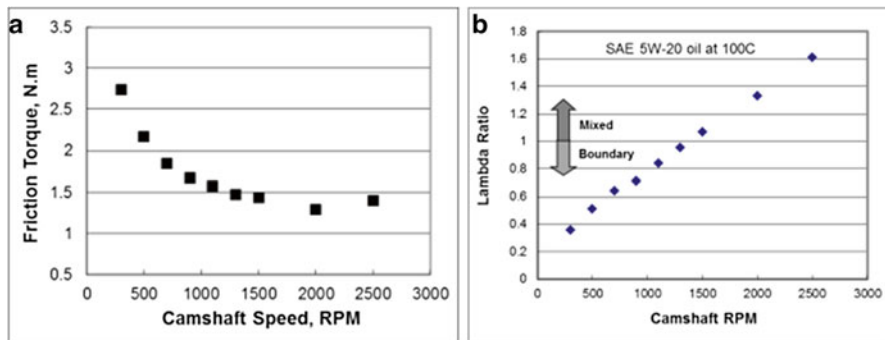
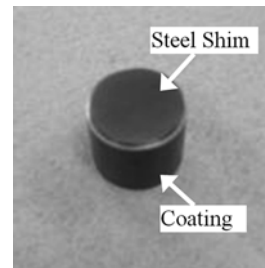


Fig. 4.3 (a) Typical valvetrain friction plot at 100 °C oil temperature, (b) Lambda ratio (i.e., lubricant film thickness divided by the average RMS surface roughness) in cam-tappet contact at 100 °C with production finish

Fig. 4.4 Design of an aluminum tappet



Tappets can be made of either steel or aluminum for weight reduction. For aluminum tappets, a steel shim is used on the top surface in contact with cam lobe to bear the high load. The cylindrical surface of aluminum slides against the bore which is the cylinder head material mostly aluminum. Although a thin oil film exists between the two surfaces, there are evidences of contact at the top and bottom end of tappet with the bore, and therefore, wear protection is necessary. Iron spray coating [2] is generally used for protection against wear and scuffing as shown in Fig. 4.4. Aluminum tappets have been used in many high volume engines in the mid-1990s.

Improvements in design and material made steel tappets similar in weight to aluminum tappets. The construction could be either two piece with a removable shim or one piece. Figure 4.5a shows an image of a single piece steel tappet and a typical camshaft with six cam lobes. Figure 4.5b and c shows a schematic drawing of the tappet construction. No coating is required on the cylindrical surface of a steel tappet, but a coating may be used on the top surface of the tappet for friction and wear reduction.

The two most widely used coatings on the top surface of a bucket are manganese phosphate and diamond-like carbon coatings, the latter is used in more recent years. Figure 4.6 shows images of steel tappets with two types of coatings. Manganese phosphate coating is deposited by an electrochemical process [3] and is generally

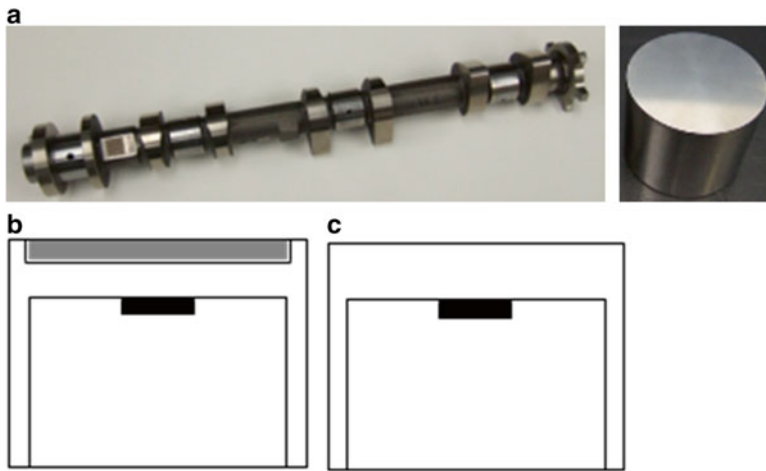


Fig. 4.5 (a) A typical camshaft and a tappet. A schematic drawing showing construction of a (b) two-piece tappet and (c) single-piece tappet

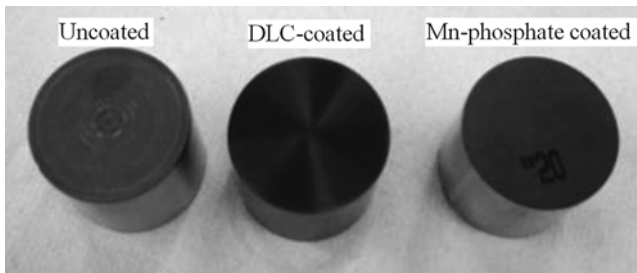


Fig. 4.6 Images of uncoated, DLC-coated, and Mn-phosphate-coated steel tappets

4–6 μm thick. The coating consists of relatively large Mn-phosphate crystals, and hence, the coatings tend to be rough (typical R_a —1.7 μm). However, this coating is primarily used as a break-in coating to ensure proper contact between tappets and the cam lobes. Diamond-like carbon coatings can be deposited by a wide variety of techniques including physical vapor deposition, chemical vapor deposition, ion beam, etc. Also there are different types of diamond-like coatings including amorphous, hydrogen containing, hydrogen-free, many may contain elements like silicon, tungsten, etc. Each of these variations of diamond-like carbon films is developed to improve specific coatings properties, i.e., hardness, friction coefficient, toughness, and thermo-oxidative behavior. Figure 4.7 shows a comparison of friction behavior of manganese phosphate and diamond-like carbon coatings in a motored valvetrain test using a production cylinder head. In these tests, one camshaft containing six cam lobes was rotated against six coated tappets. Both coatings showed friction reduction compared to uncoated tappets at all temperatures investigated. Although DLC-coated

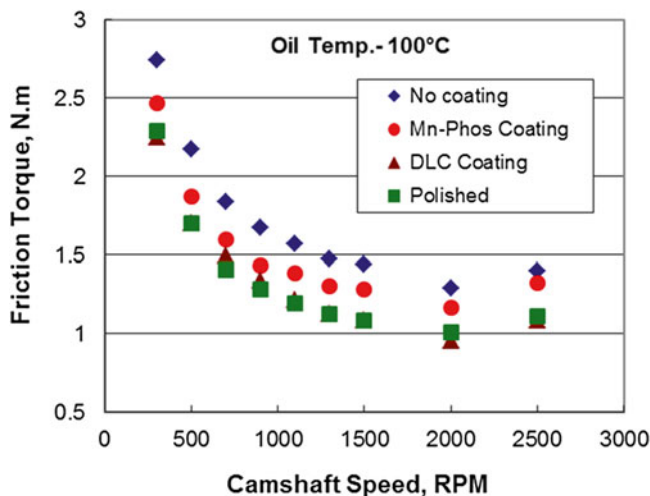


Fig. 4.7 Friction reduction potential of tappet coatings

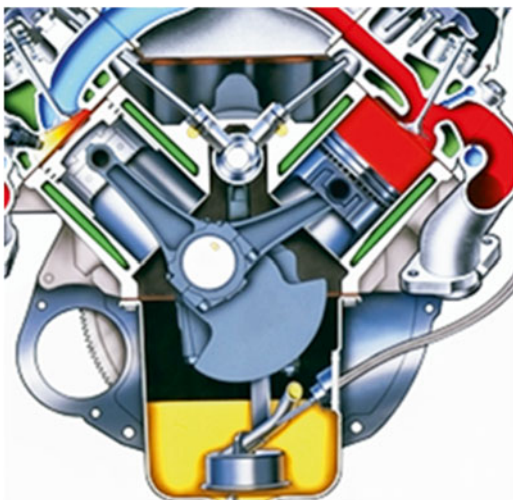
tappets showed similar friction reduction capability as polished tappets, there are other variants of DLC coatings which did show improved friction reduction. The results also depend on the design of the valvetrain i.e., spring load, design of cam lobes, type of oil used, etc. The same DLC-coated buckets showed much higher friction reduction in another engine.

Nissan first introduced hydrogen-free DLC-coated tappets in their 2.5 L and 3.5 L V-6 gasoline engines for friction reduction [4, 5]. Volvo's new four cylinder gasoline engine architecture will use DLC-coated tappets [6]. However, one of the considerations for diamond-like carbon coatings is compatibility with engine oils. Oils containing molybdenum dithiocarbamate as a friction modifier did not show friction reducing effect with diamond-like carbon coating [7]. There are several papers documenting that oil containing molybdenum dithiocarbamate friction modifier increased wear of DLC-coated disks [8–11]. The mechanism appears to be that decomposition of MoDTC produced MoO_3 , which interacted with the DLC coating, resulting in increased wear. Polished valve lifters are also used for friction reduction, but the surface is protected by a thin layer of chromium nitride coating for anti-wear and anti-scuffing characteristics [12].

4.3 Piston Ring/Cylinder Bore System

The primary purposes of the piston ring are to hold the combustion pressure by sealing the interface with cylinder bore surface and to minimize leakage of combustion gases through the clearance between the piston and the bore. A secondary function is to scrape oil from the cylinder bore surface to minimize transportation to the

Fig. 4.8 A view of the cylinder block showing various engine components including pistons, piston rings, connecting rod



combustion chamber where it can burn and contribute negatively to exhaust emissions. Most of the gasoline engines have three piston rings: top compression ring, second compression ring, and the oil control ring (Fig. 4.8). The sliding of the ring pack against the cylinder bore surface results in significant energy loss due to friction. The sliding movement is also associated with wear of piston rings and cylinder bore surface. Scuffing is another failure mode at this interface. Therefore, materials selected at this interface should provide low friction for improved fuel economy and reduced wear and scuffing for durability over a wide operating temperature range (-40°C to 300°C).

It is important to understand the load, speed, and lubrication regime for better appreciation of material requirements. The primary load acting on the top compression ring is the pressure spike generated from the combustion of fuel and air mixture. Figure 4.9 shows typical combustion load acting on the top compression ring, second compression ring, and the oil control ring. The pressure spikes a few degrees after the top dead center position in power stroke after which it drops rapidly until the end of the compression stroke. The peak pressure on the second ring is much lower and broader than the top compression ring. The oil control ring experiences the least pressure.

In addition to combustion load, the rings also exert axial force on the cylinder bore surface called ring tension which seals the interface and prevents leakage of combustion gasses. The ring tension is determined by the geometry of the rings. The ring tension on top compression and second compression rings is nearly the same, about 5–10 N range, but the oil control ring is higher, 15–30 N, for gasoline engines. The ring tension is carefully balanced as higher ring tension prevents oil transportation to the combustion chamber but increases friction, and vice versa.

Figure 4.10 shows the distribution of minimum oil film thickness during the four strokes of a gasoline engine at two different speeds. The oil film thickness is highest

Fig. 4.9 Gas pressure distribution as a function of crank angle at 2,000 RPM in an engine

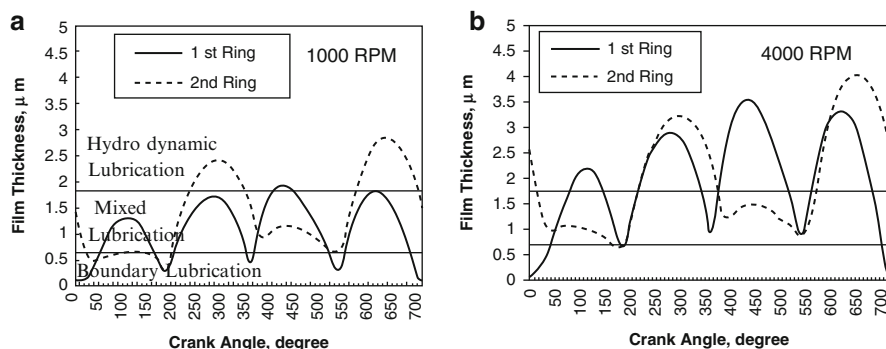
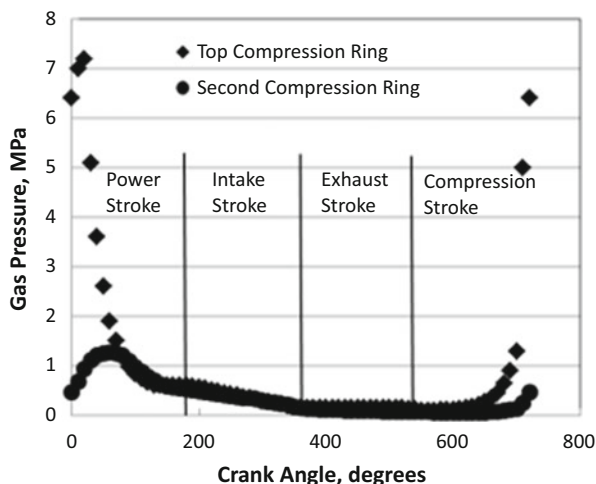


Fig. 4.10 Film thickness distribution as a function of crank angle at (a) 1,000 RPM and (b) 4,000 RPM

at the middle of the stroke and at higher speed as expected. Also, the oil film thickness is lower during the power stroke because of the high gas pressure. The oil film thickness at the second compression ring is lower than the top compression ring during the power stroke. The surface roughness (R_q) of typical cylinder bore and piston ring surfaces are $0.50\text{ }\mu\text{m}$ and $0.3\text{ }\mu\text{m}$, respectively, which lends a composite surface roughness of $0.6\text{ }\mu\text{m}$. Two lines are drawn on each figure at film thicknesses which correspond to specific film thickness (λ) of 1 and 3, thus separating boundary, mixed and hydrodynamic lubrication regimes. It can be observed that the top compression ring operates under boundary and mixed lubrication regimes at 1,000 RPM even at the middle of the stroke. But at 4,000 RPM, the top compression ring operates under hydrodynamic regime for a significant part of the stroke. The second ring operates similarly. Therefore, depending on the engine speed and oil temperature,

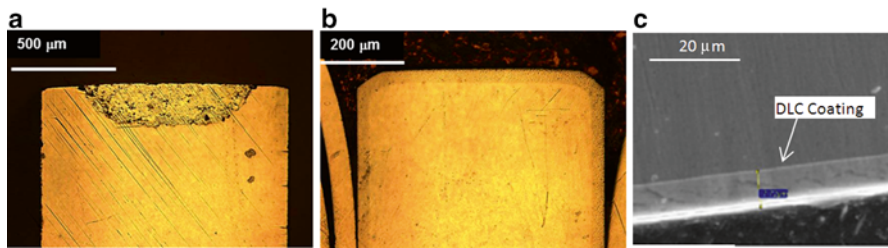


Fig. 4.11 Top compression ring coatings; (a) Mo-NiCr coating, (b) nitrided, and (c) DLC coating

the rings may operate under boundary and mixed lubrication regime, and therefore, coatings play a role in enhancing friction and wear performances.

Top compression ring—the top compression ring is generally barrel faced as shown in Fig. 4.11, and several coating materials could be used. One common design is to fill the middle portion of the ring with Mo-NiCr material deposited by plasma process [13]. The primary purpose of this coating is to optimize friction, wear, and scuffing performances. In another design, the top compression ring could be nitrided as shown in Fig. 4.11b. Thin film coatings such as chromium nitride [14–16] and diamond-like carbon [17, 18] have been developed and are increasingly used [19]. These coatings are typically deposited by physical vapor deposition techniques. Figure 4.11c shows a typical DLC-coated top compression ring.

Oil control ring—the primary purpose of the oil control ring is to scrape oil from the liner surface down to the oil sump and prevent oil from going to the top of the liner. This is generally achieved by increased ring tension. Higher ring tension is also associated with higher friction and wear, and therefore, a balance is to be maintained. The oil control rings can be nitrided, chrome plated, or CrN and DLC coated [19].

Cylinder bore coating—in automobile engines, cast iron cylinder blocks and cylinder heads have been used for a long time. Over the last 20 years, the cast iron heads have been replaced with aluminum heads for weight saving. Similarly cast iron cylinder blocks have been replaced with aluminum. However, aluminum alloys do not show acceptable wear behavior in contact with ferrous-based piston rings under engine operating conditions. Therefore, a cast iron liner or sleeve is either cast-in or pressed-in on aluminum cylinder blocks. The current trend is toward replacement of cast iron liners with deposition of an iron-based coating on aluminum cylinders to reduce mass and improve fuel economy.

Two types of bore coatings are of interest currently: thermal spray coatings and electrolytic plasma oxidation coatings. Thermal spray coatings are deposited by a family of processes that uses a concentrated heat source either by using an electric arc or plasma arc or combusting a gas mixture, passing gas with high kinetic energy through the heat source, and melting the materials to be deposited. The molten material is carried by the gas and deposited on to the substrate where they rapidly solidify. The kinetic energy is provided by constricting the flow of the gas through a nozzle, and it is high enough to transport molten particles at supersonic speed to

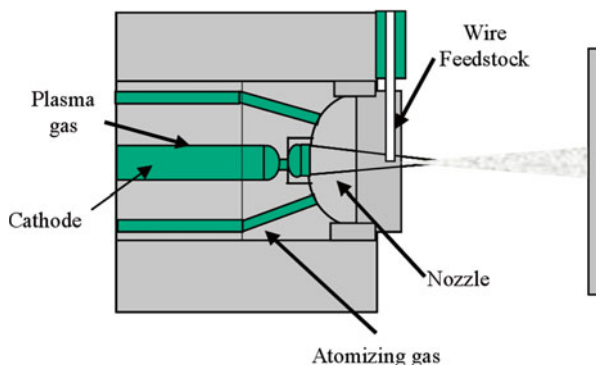


Fig. 4.12 A schematic drawing of plasma transferred wire arc process

the substrate. This leads to very high deposition rate and allows deposition of thick coatings (100–300 μm). Also, thermal spray is a “line-of-sight” process where the stream of molten droplets deposits only on to the surface that is directly in line with the spray stream. One of the advantages of thermal spray process is that the substrate undergoes minimal heating or some local melting. Therefore, the substrate chemistry or mechanical properties like hardness do not change appreciably. The bonding between the substrate and coating tends to be mechanical interlocking caused by the impingement of molten droplets at supersonic speed on the substrate surface. Therefore, surface preparation is the key to achieving the desired bond strength.

Plasma transfer wire arc (PTWA) is one of the thermal spray processes, and the technology has advanced to a stage that it is now used in production engines. The deposition rate achieved by this process is much higher than that achieved with conventional plasma spray process and also at a lower power level. Figure 4.12 shows a setup of the process. It consists of a torch head attached to a spindle, which is rotated by a motor. The torch head consists of a nozzle through which a plasma gas flows surrounding a copper cathode. The plasma gas could be argon or nitrogen. The wire feedstock acts as anode and is pulled within the torch head perpendicularly and in front of the nozzle cone. The plasma is created by applying a voltage of 100–120 V and 60–100 mA current between the tip of the cathode tube and the anode feedstock. These conditions raise the temperature high enough to melt the wire materials. The flow of the plasma gas and the atomizing gas, which could be compressed air, detaches the particles from the anode tip and forces it to the substrate on which the coating is desired. The flow of plasma gas and the atomizing gas is maintained such that the particles travel at a high speed (100–130 m/s), creating a dense coating. However, for coating the cylinder bore of an automotive engine, the spindle needs to rotate vertically at the center of the cylinder bore and then honed to the desired specification. The coating deposition process requires mechanical roughening of the substrate to improve the bond strength. In a slightly different setup, two different wires could be used as well and the method is called twin-wire arc process. Figure 4.13 shows image of a PTWA-coated engine block.



Fig. 4.13 Photograph of an engine block cross section showing (a) cast iron and (b) PTWA surface following honing

The typical coating thickness is about 200 μm . Since the coating thickness increases with time, a layered structure is developed with low porosity (2–3 %), and therefore, the as-deposited coating tends to be rough. The coating is finished with honing. The coating composition and hardness are controlled primarily by the composition of wire feedstock, which is typically low to medium carbon steel for automotive engine applications. The process is being used in production engines by Ford since 2009 [20]. Recent work showed a higher porosity PTWA offers improved friction benefits [19, 21]. A slight different process called twin-wire arc spraying is developed by Daimler and is used in diesel engines since 2010 [22]. The cylinder surface is smooth hone finished and optimized with appropriate piston ring material resulting in reduced friction by reducing ring tension. BMW developed a similar but slightly different technology called electric arc wire spray (EAWS) for the 2.0 L I-4 engine [23].

High-velocity oxy-fuel is another thermal spray process which consists of feeding a mixture of oxygen and an oxy-fuel at high pressure into water-cooled combustion chamber. Following combustion, the resulting flame/gas stream is passed through a confined nozzle. The coating material is fed through a carrier gas either at the tip of the nozzle in a powder form or through the center of the gun depending on the design. The coating powders melt at the high temperature generated at the nozzle tip, and molten droplets are carried by the gas stream at a high velocity (300–600 m/s) toward the substrate material. The molten powder particles solidify upon impingement on the substrate surface. The high kinetic energy of particles leads to extremely dense coatings [24, 25]. The high hardness and high oxide content demands appropriate

matching with piston ring material. However, this technology has not reached a stage for implementation on automotive engines.

Electrochemical cylinder bore coatings were developed in the early 1990s to address higher wear of rings, cylinder bore, and bearings with methanol fuels than gasoline-fueled engines [26]. These coatings were also developed to be applied directly on an aluminum engine cylinder bore to avoid use of cast iron liners. These coatings were appropriate because of their higher wear resistance and lower friction coefficient than cast iron. Nickel composite coatings are attractive because of precision-controlled low-temperature operation, low-cost and low energy requirements, high deposition rate, and the ability to deposit on complex geometry [27]. Nickel composite coatings are deposited by electroplating technique. It consists of a plating bath with an anode and a cathode with an electrochemical solution. The anode is made of nickel and the cathode is made of the material on which the coating is to be deposited. The electrochemical solution is made up of nickel sulfate or ammonium sulfate, nickel chloride, and boric acid. A second phase is often added to tailor the properties of the coating for improved wear resistance, friction coefficient, and corrosion resistance. The most common material is electroplated nickel with embedded silicon carbide particles and is commonly known as Ni-SiC or Nikasil coating. However, these coatings fell out of favor because of environmental compatibility (disposal of nickel) and incompatibility with high sulfur fuel in certain regions in the world.

Plasma electrolytic oxidation coatings show more promise today. It is similar to anodization process but done. At a higher voltage (250 V), and with a suitable electrolyte, creating plasma discharges at the interface. These discharges are short-lived, often in the range of nanoseconds to milliseconds, and the sizes of these discharges are very small, in the range of 100–300 μm [28]. The process is also described as plasma anodizing, microarc anodizing, spark anodizing, or arc anodizing. The coating growth takes place in the regions of microdischarges. Figure 4.14 shows a schematic description of the plasma electrolytic process. Yerokhin et al. provided a detailed review of the process [29]. The coating generally forms two layers; the top layer (10–20 μm) is called a loose layer containing large pores and can be removed by machining or could be impregnated with other materials to impart specific property like reduced friction by incorporating solid lubricants like graphite or molybdenum disulfide [30]. The layer closer to the substrate, which could be as thick as 100–200 μm , is the actual functional layer for tribological application or corrosion protection with low porosity. The coating is essentially alumina and the hardness of the intermediate layer is about 900–2,000 HV. Plasma electrolytic oxidation process is currently used in automotive pistons and brake components for improved wear and corrosion characteristics. However, the technology is still under development for cylinder bore application.

Piston pins—the motion of the piston pin is complex and studied by several authors [31, 32] experimentally and analytically. Abed et al. [31] through a motored laboratory rig demonstrated that piston pin rotates partially and slowly depending on load acting on the connecting rod. Shi [32] showed through analytical models that friction force on the piston pin could be quite high. Therefore, an opportunity

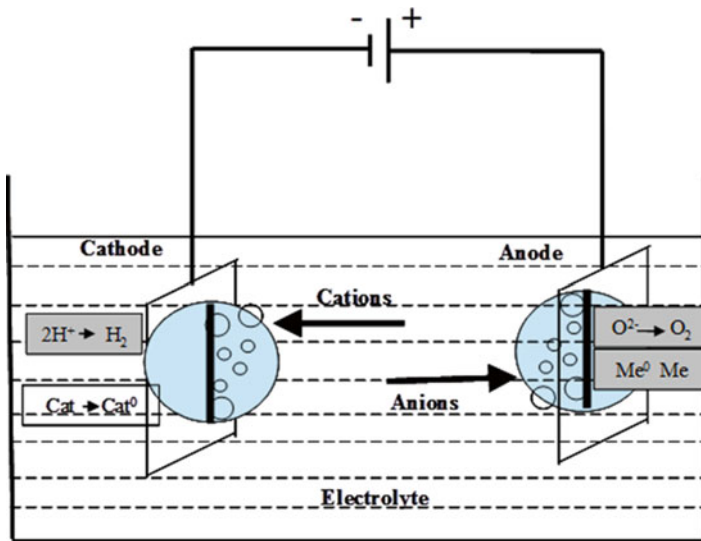


Fig. 4.14 A schematic drawing of plasma electrolytic process

lies for friction reduction through coating. Diamond-like carbon (DLC) coatings are being used on piston pins in recent engines [6, 21, 34]. DLC coating on piston pin may have an added advantage of reducing piston skirt friction by altering the piston motion [33].

Piston skirt coatings—the piston skirt and cylinder liner contact operate primarily in hydrodynamic lubrication regime when the piston is moving straight on the bore. However, due to the cranking mechanism, the piston skirt comes in contact with the bore at the top and bottom dead center areas. Also, at the operating temperature, the expansion of the aluminum piston reduces clearance and hence opportunities for contact. The friction, wear, and noise associated with contact are reduced traditionally by applying a thin coating on the skirt area. It is typically a polymer-based, mostly polyamide-imide, bonded coating with solid lubricant particles (graphite and/or molybdenum disulfide) which can be applied either by spray method or screen printing method and requires curing with heat following deposition. Figure 4.15 shows a typical coating on a piston skirt. The coating can be typically about 20 μm thick. The coating technology continues to evolve to improve friction reducing capability by adding nano-diamond particles [34] or nylon particles [35] or carbon fibers [36] while making the coating deposition process more environment friendly or less expensive. Ogihara [37] explored friction reduction opportunity by a microdimple technique where the piston skirt surface was blasted with compressed air with ultrafine flattened MoS_2 particles. This process resulted in embedment of MoS_2 powder on the surface and inside the parent metal. The local temperature increase caused formation of intermetallic phases due to reaction

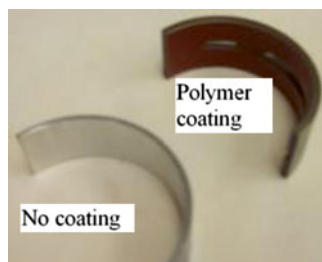
Fig. 4.15 Piston with coating on the skirt area



with parent aluminum surface. Significant friction reduction was observed both in laboratory bench and engine tests. Honda 2.4-L engine used a unique dot pattern coating on the outer skirts of the piston [38]. Piston manufacturers have developed their own proprietary coatings such as EcoTough [39] and Nanofriks [40].

Bearings—the bearings in internal combustion engines should have good fatigue strength to withstand repeated loading and unloading resulting from combustion cycles. In addition, bearings should also have good seizure resistance because of the high load acting on it. Traditionally, bearing consisted of a steel backing plate with copper-bearing material layer with a lead-based overlay. Lead is used because of its excellent lubricity and the ability to embed any hard particles being carried by the lubricant. However, due to legislation, the use of heavy metal (lead) has been stopped. This leads to the development of lead-free bearing materials with silver-bismuth used as an overlay [41, 42]. The designing of bearing materials is becoming more challenging because of more aggressive operating environments demanded with advances in engine technologies, i.e., turbocharging, and start–stop feature to improve fuel economy. Bearings in turbocharged engines experience higher loads at low speeds than conventional engines. In addition, turbocharged engine also experiences higher fuel dilution (3–4 %) which lowers lubricant viscosity and thus the minimum oil film thickness. Start–stop cycle forces the bearings to operate in low speed regime more frequently than those experienced without this feature. Both conditions allow bearing to spend more time in mixed and boundary lubrication regimes. The proliferation of flexible fuel vehicles using ethanol blend fuels has also shown signs of bearing corrosion. All these factors require bearings to be more robust. To address these issues, a polymer coating has been developed which can be applied on aluminum alloy or copper alloy layer with a steel backing plate. Figure 4.16 shows images of a polymer-coated bearing. The polymer coating is composed of high-performance polyamide-imide resin which provides excellent high-temperature stability and corrosion resistance. The polymer layer is often mixed with solid lubricants like graphite, molybdenum disulfide to provide low friction, and metallic or oxide particles to provide strength and wear resistance. An adhesion agent is also added to promote bonding with the metallic lining underneath [43, 44].

Fig. 4.16 Images of an uncoated and a polymer-coated bearings



4.4 Summary

Coatings have a great role to play in engine components and often thought as a potential solution to address issues related to friction, wear, and corrosion. Coating technologies evolved as engine technologies changed, and concern over environmental issues related to handling and disposal of chemicals, and reducing dependence on foreign oil continued to rise. Use of methanol blend fuels was very much favored in the late 1980s to reduce consumption of petroleum fuels which led to the development of electrochemical coatings to address cylinder bore corrosion. Also, focus on alternative fuels changed to ethanol from methanol. Later, disposal and handling of chemicals became an issue, leading to the development of plasma spray coatings for cylinder bore and piston rings to improve wear resistance and scuffing. As fuel economy improvement became a major issue in the late 1990s, significant efforts were made to develop low friction thin coatings. A specific example is research on development of diamond-like carbon coatings which was really intensified starting the mid-1990s for its friction reduction and improved wear resistance capabilities. After nearly 20 years, these coatings are being used in mass-produced engines. Similarly, polymer-coated bearings are used as engine technology changed to turbo-charged direct injection delivering more torque at low speeds and improving fuel economy at the same time. Also, advancement of start/stop technology to improve fuel economy necessitated the use of these coatings for improved durability. As improving fuel economy remains a major focus for the automotive industry in the years ahead, friction reduction through coatings will be important. Also, as engine technologies improve, more durability-related issues may arise which can be addressed by coatings. Therefore, challenging and exciting times are ahead for coating development and its application.

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Chapter 5

Customized Coating Systems for Products with Added Value from Development to High-Volume Production

T. Hosenfeldt, Y. Musayev, and E. Schulz

Abstract Modern components and systems for automotive and industrial applications have to meet various requirements in multiple technical fields. Apart from properties that affect the part itself—like geometry, stiffness, weight, or rigidity—the surface properties must be adjusted to the growing environmental requirements. Therefore, coatings are increasingly applied to reduce the friction losses of car components, improve fuel efficiency, and reduce CO₂ emissions. This article describes how to use surface technology as a modern design element for components and systems to enable the demanding requirements on market-leading automotive and industrial products. Therefore, Schaeffler has developed and established a coating toolbox for customized surfaces to deliver the right solutions for all that needs and requests with the corresponding coating system enabled by PVD/PACVD, spraying, or electrochemical technology. For innovative products, it is extremely important that coatings are considered as design elements and integrated in the product development process at a very early stage. In this article, tribological coatings are viewed within a holistic and design-oriented context. The latest developments of amorphous carbon coatings and their characteristics and the technical and economical effects of their use in combustion engines and industrial bearing applications are described. The presented Triondur® amorphous carbon-based coating systems (a-C:H, a-C:H:Me, a-C:H:X, and ta-C) are excellent examples for customized tribological systems like bucket tappets or roller bearings. These carbon coatings offer the following advantages: super low friction with highest wear resistance, customized surface energy, optimized wet ability and interaction with formulated engine oils, and low adhesion to the counterpart.

A close collaboration between designers and surface engineers is required in the future. Schaeffler delivers around 100 million high-quality PVD- and (PA)CVD-coated components every year that enable outstanding applications, preserve resources, and meet increasing customer requirements.

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Keywords Tribology • Interactions • Amorphous carbon coatings • Prediction of friction • CO₂-Efficiency

5.1 Motivation

Today CO₂ reduction is often used as a synonym for friction reduction in the automotive industry. Above all, legislative guidelines, for example, those of the European Union, to regulate CO₂ emissions and fleet consumption of automobile manufacturers are the driving forces for the improvement of energy efficiency and durability of modern gasoline engines [1]. This means that it is getting more and more important to reduce friction and wear in highly stressed contacts of combustion engines. Therefore, the application of amorphous carbon coatings, used for example in the valve train, is in demand. In such tribological systems, the part, counterpart, intermediate, and environment each interact with one another in a manifold manner (Fig. 5.1) [2].

In the contact area between part and counterpart elementary friction and wear mechanisms such as adhesion, abrasion, surface fatigue, deformation, elastic hysteresis and damping, tribochemical reactions, etc. may occur. These mechanisms are overlapping in the temporal and spatial undetectable real material contact area. In addition highly formulated lubricants, which are mainly used with highly stressed engine elements, exert influence on tribochemical reactions inside and outside of the tribological contact [2].

Due to these various reciprocal effects, the behavior of such tribological systems becomes very complex, which means that the theoretical prediction of friction and wear is hardly possible at present. Therefore, during development and/or optimization of each tribological system, always experimental investigations mostly based on empirical knowledge are conducted. Thereby normally, the focus is only on one machine part or even exclusively on the coating. Ideally, such investigations are carried out on test rigs, which reproduce the real system as close as possible, for example, on a driven cylinder-head test rig, to investigate the behavior of the machine part

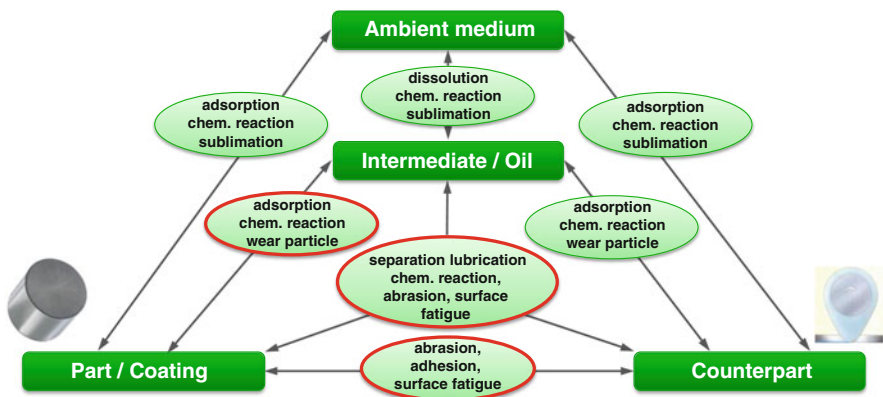


Fig. 5.1 Interactions in tribological system [2]

respectively to the coating under real boundary conditions. However, such experiments are associated with a high temporal and financial effort. This often leads to the application of abstracted, cheap, and time-effective model tests or component tests like the ball-on-disk tribometer. However, the transferability of these tests to the application is restricted. This indicates the need for a suitable method to predict the friction and wear behavior of tribological systems containing tribological coatings. With this development, the time and the amount of expensive tribological tests can be reduced.

5.2 Amorphous Carbon Coatings

Since the mentioned interactions take place mainly at the surface of contacted components, friction and wear can be influenced by surface modification like structuring and coating. By coating the ground part for example, a further element is added to the structure of the tribological system (Fig. 5.2) [3]. These surface modifications have to be adapted to the respective application and should be taken into account during the design phase of the tribological system, so the coating should be seen as a design element.

Amorphous carbon coatings are in particular suitable for this purpose since its properties can be adjusted for different requirements. These characteristics are founded on its bonding structure and hydrogen content. Amorphous carbon coatings consist of notably stable diamond-like tetrahedral sp^3 -bonds, which ensure a high wear resistance, and graphitic sp^2 -bonds that enable a slight slipping between the atomic hexagonal-structured planes [4, 5]. Regarding its structure and its properties, amorphous carbon coatings can be located in a triangle between graphite, polymer, and diamond.

Depending on the manufacturing process, the coating parameters, and the exact composition, it is possible to adjust the properties of the coatings up to the edges of the triangle. In addition, the chemical structure and polarity of the coating and thus

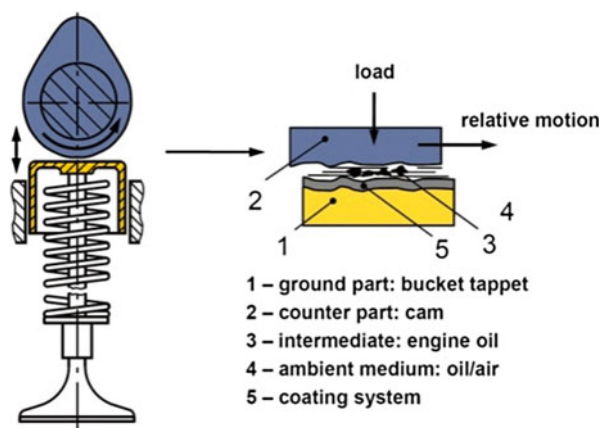


Fig. 5.2 The five elements of a tribological system [3]

the reactivity with surface-active additives can be influenced by doping the coating with metals (Cr, W, Ti,...) or nonmetals (F, O, Mo, Si,...) [4]. Schaeffler has developed a coating toolbox with tailored Triondur® amorphous carbon-based coating systems (a-C:H, a-C:H:Me, a-C:H:X, and ta-C) as a modular design element for customized tribological systems with low friction and highest lifetime.

The advantages of amorphous carbon coatings under dry conditions are the low friction coefficient of about 0.1–0.2 in combination with high wear resistance [5]. In lubricated tribological systems working under mixed friction conditions, the performance of amorphous carbon coatings depends on the interaction between all elements of the tribological system. Concerning its additive composition, current engine oils are optimized for steel/steel contacts. Accordingly, the chemical and physical behavior of additives, like antiwear agents, extreme pressure agents, and friction modifiers, in contact with steel is well known. If however engine parts are coated with amorphous carbon coatings, the chemical behavior of one element changes and therefore the behavior of the whole tribological system. The reason for this is that these additives (e.g., Mo-DTC, Zn-DTP, etc.) cannot completely take effect on the inert and nonpolar carbon surface. Through the changed reaction conditions, even undesirable effects may occur leading to an increase of friction and wear [6, 7].

5.3 Prediction of Friction and Wear

The goal during an application-based and market-oriented development of tribological coatings for reduction of CO₂ emissions is to provide a coated system solution respectively coated components with a maximum of customer benefit as quick and cost efficient as possible. To reduce development time and coating cost, the lubricant and counterpart need to be adjusted purposefully to the particular application. This means for the system bucket tappet/camshaft that with a given component—for example, camshaft, lubricant, or coating—a recommendation for the design of the remaining components can be given.

One possibility to achieve this goal is the isolated determination of single effects as published in [6–13]. Thereby the single effects are observed under fixed boundary conditions realized by abstraction and simplification of the tribological system in order to handle the complexity of the tribological processes.

Thus, in [6], the reactivity of the antiwear agent Zn-DTP could be verified on an amorphous carbon coating containing hydrogen by the use of a ball-on-disk tribometer with rotating disk and an additional XPS analysis. However, the adhesion strength of the resulting tribofilm was considerably weaker than on a steel surface. As a result, the wear-reducing effect of Zn-DTP cannot occur, and on the contrary, hard wear-promoting particles are brought into the tribological contact by delamination of the reaction layer. Moreover, the formation of a reaction layer by Zn-DTP requires energy, which leads to an increase of the friction coefficient up to the level of the steel/steel contact [6]. However, it is possible to achieve a significant friction reduction in the range of fluid friction with hydrogen-free carbon coatings when the

lubricant is adjusted to the carbon surface. In [8], it was found that special friction modifiers are especially effective with tetrahedral hydrogen-free amorphous carbon coatings (ta-C). In a ball-on-disk tribometer with oscillating ball, ta-C-coated disk, and GMO-doped base oil, friction coefficients below 0.02 were reached. This extreme low friction is explained by the hydroxylation of the ta-C surface leading to low shear forces in the interface between the coating and lubricant [8]. With amorphous carbon coatings containing hydrogen, such a drastic friction reduction was not yet reached. In [7], various amorphous carbon coatings were investigated with a lubricated block-on-ring test lubricated with a Mo-DTC friction modifier-doped base oil. Here, it was found that Mo-DTC decomposes in the tribological contact under generation of MoS_2 and MoO_3 . Although the friction coefficient was reduced with most amorphous carbon coatings, a rise in the wear amount was observed. MoO_3 seems to promote the oxidation of the amorphous carbon coatings [7].

These described investigations were often carried out with model tests like pin on disk, which can be carried out quite easy, but the results are often far away from the real application. On the other hand, aggregate and field tests have a much better transferability to the application, but it is to be expected that these tests are more expensive and time-consuming.

Just in such tribological systems like the contact between cam and coated bucket tappet with lubricants containing additives, it is quite possible that results out of different categories can be contradictory. This was proven in [14] by carrying out experiments with different amorphous carbon coatings on a ball-on-disk tribometer and a driven cylinder-head rig, whereby no correlation between the results could be found. So based only on model tests, it is not possible to fathom out all effects and superimpositions for a transfer to the real system cam/bucket tappet. Up to now, this transferability can only be ensured when aggregate tests or even field tests are applied, whereby the financial and temporal efforts become disproportionately high. But by applying statistical methods with learning capabilities, the experimental effort can be reduced significantly. Thereby it is possible to determine expected output variables from given input variables. For example, artificial neural networks allow a quite good prediction of friction and wear on the basis of a large amount of experimental data.

5.4 Data Collection

A predictive modeling requires the availability of a sufficient large amount of empirical test data. For this database already existing test data from a driven cylinder-head test rig were pulled up. Furthermore, a multitude of experiments was carried out by a systematic variation of the explanatory variables with a ball-on-disk tribometer. As already mentioned, there is an obvious discrepancy between the results of these two tests. Therefore, a novel valve train test rig, which should close the gap between the model test and the aggregate test, was used. It is designed as a single-valve test rig and reproduces the system cam/bucket tappet as realistic as

possible. Thereby a genuine camshaft section with the associated bucket tappet and valve spring is used. This valve train model test rig provides the opportunity to determine the friction and normal forces appearing in the tribological contact separately. The used database generated with all these different tribological methods includes a total amount of 262 experiments (NDO).

In case of the tribological contact between cam and coated bucket tappet, the output variable is the friction coefficient. The input variables are the type of coating, hardness, Young's modulus, and surface roughness. Thereby aside from uncoated bucket tappets and a nitride chromium hard coating, six different amorphous carbon coatings were investigated. The used amorphous carbon coatings differ in their hydrogen content and their doping elements. The lubricant additives and their concentration and the base oil and its viscosity were added to the database as well. Here, PAO and mineral base oils as well as the additives Mo-DTP, Zn-DTP, and GMO were taken into account. Furthermore, the stress parameters of the tribological experiment were varied as input variables, so do relative velocity, oil temperature, and contact pressure. The reproducibility of the friction measurements was determined by repeating a measurement several times at the same conditions. These results show that the relative variance of these measurements is in a range of about 5 % of the friction value.

5.5 Applications

With the holistic competence in surface technology, we offer prediction and optimization of tribological systems, design of the tailored coating system and its production process for components with added value for the customer and society for automotive as well as industrial applications.

The valve train is one of the main elements of combustion engines and is closely involved in the friction losses of the combustion engine [15]. The valve train can assume several designs depending on the position of the camshaft and design of the cam follower. Above all, the mechanical bucket tappet and the roller finger follower are at present the most common valve train systems [16]. With the roller finger follower, the contact between cam and follower is designed as a rolling contact with low friction losses. However, the realization of a rolling contact is considerably more expensive [15, 17]. This is reflected in the cost-benefit ratio as well (Fig. 5.3).

Here the basis with 0 % friction reduction and 100 % costs is represented by the carbonitrided and tempered mechanical bucket tappet. A friction reduction of about 25 % can be achieved by an optimized surface treatment of the standard bucket tappet. An additional reduction of friction down to the low level of a roller finger follower is possible by the application of a tailored coating (Fig. 5.3) [17].

With an adjustment of all components, for example, the best coating for the respective lubricant or the respective cam and cam structure, it is possible to reduce the friction level down to 50 %, which means lower CO₂ emissions of 1–2 %.

Legislative guidelines will increasingly influence this cost-benefit approach [1]. With this, the greater expense for coating engine parts can be amortized by the reduction of CO₂ emission.

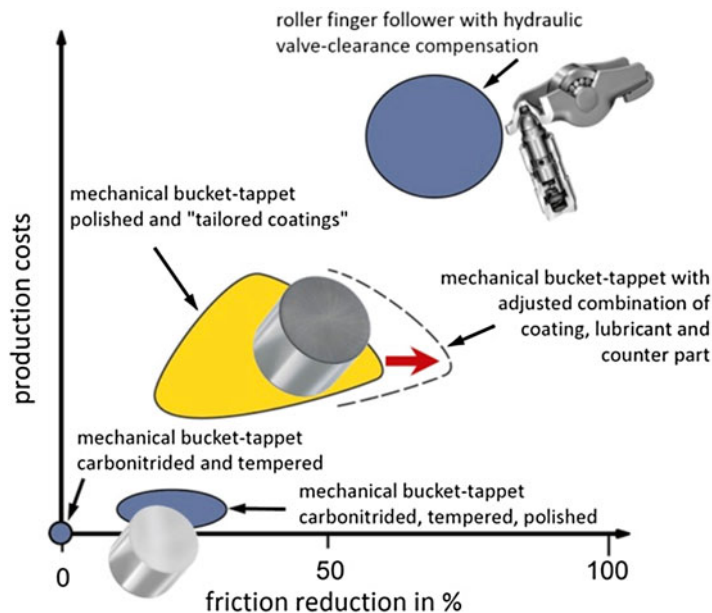


Fig. 5.3 Cost-benefit ratio of different valve train modifications according to [17]

Energy efficiency is getting also more and more important in industrial applications and the operational areas are facing tougher challenges. Therefore, Triondur® coating systems have gained attention as a modular and successful design element in product development to reduce the friction losses and enhance the operational area, respectively, and the lifetime of bearings. With a tailored Triondur® DLC coating system, it is possible to reduce the friction in barrel rollers under poor lubrication, nearly independent from the load of about 40 %.

In other words, such coating systems enable the same low friction under poor lubrication than standard bearings under good lubrication (Fig. 5.4).

5.6 Conclusion and Outlook

A close collaboration between designers and surface engineers is required in the future. With the Global Technology Network, Schaeffler is combining its existing local expertise in the regions with the knowledge and innovative force of its experts all over the world. Schaeffler is strengthening its local expertise and bringing engineering and service knowledge even closer to its customers through the introduction of Schaeffler Technology Centers and collaboration in global expert networks. Customers all over the world benefit from this and receive innovative, customized solutions of the highest quality.

Schaeffler delivers around 100 million high-quality PVD- and (PA)CVD-coated components (Triondur®) every year that enable outstanding applications, preserve

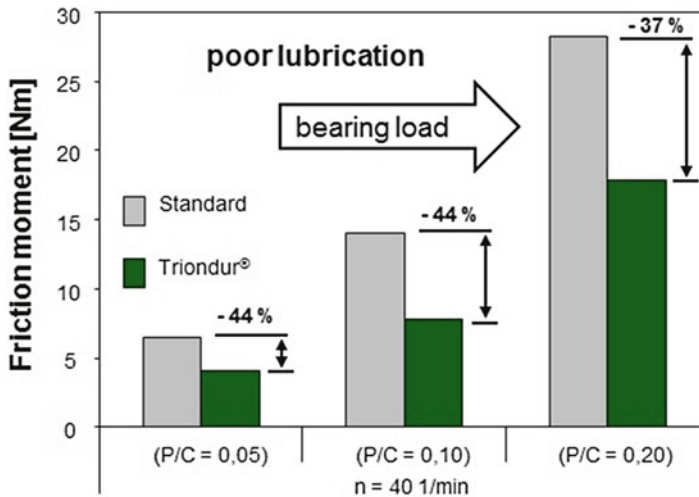


Fig. 5.4 Friction reduction in barrel roller bearings with Triondur® coating systems under poor lubrication

resources, and meet demanding customer requirements. In order to reduce the temporal and financial effort for tribological experiments, a prediction of the friction behavior of lubricated tribological systems containing amorphous carbon coatings should be realized. This prediction requires the availability of a sufficiently large database which contains case studies.

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Chapter 6

Surface Treatments for Automotive Applications

Jörg Vetter

Abstract Advanced surface treatments are used more and more in daily manufacturing of parts for the automotive industry to serve functional and decorative purposes. Higher specific loads (thermal, mechanical, etc.), weight and friction reduction, longer components lifetime, and improved corrosion resistance are demanding for modern automotive systems. Within the last decades, high-performance surface solutions and new or improved surface treatments, especially in the group of plasma-assisted processes, both for diffusion and deposition processes were developed to provide economic applications for automotive parts. The surface treatments PVD, PACVD, thermochemical heat treatment, and thermal spraying will be briefly described. In addition, the combination treatment involving at least two different treatments will be discussed. It will be shown that these new treatments are becoming more common in engine applications and power train. The potential of optimized functional surface generation is demonstrated both for different types of substrate materials (e.g., Al alloys, sintered steels, case-hardened steels, etc.) and part geometry (e.g., cylinder bores). Due to the fact that an enormous wide property field of surfaces is adjustable within these competing surface treatments, it becomes common to substitute the more limited traditional treatment-substrate systems (e.g., galvanizing, electroplating etc.) with the described advanced treatments. Besides a general description of the surface treatments and their main application aspects, the internal coating of bores inside the engine by plasma spraying, the increased corrosion protection of power train parts by the IONIT OX process as well as piston ring treatments, and the widespread potential for DLC coatings are discussed in more detail.

Keywords Atmospheric plasma spraying process • Automotive applications • Carbon linings • Cold plasma • Combination treatments • Corrosion • DLC architectures • Fatigue • Friction • Gas nitriding • Gas nitrocarburizing • Hard coatings • Hydrogen free DLC • IONIT OX process • LTE-plasma • Magnetron sputtering • Oxidation • PACVD process • Plasma assisted surface treatments • Plasmanitriding • Plasma nitrocarburizing • Plasma states • PVD processes • RotaPlasma • Substrate-treatment-system • SUMEBore • ta-C • Thermochemical heat treatment • Thermal spraying • Vacuum arc evaporation • Wear

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6.1 Introduction

Enterprising automotive executives have to optimize their business models constantly and improve existing technical solutions or even create new ones in order to be able to compete effectively. In addition they have to consider customers' expectations and satisfaction (which include reliability, functionality, comfort, and safety). Also, aspects such as production and environmental issues are decisive. Environmental regulations and shorter product life cycles demand higher quality and more stringent material selections. Surface enhancement engineering solutions of tribological systems (engine, transmission, drive system) are often a demand of the automotive industry, and even the protection against corrosion for selected components has to be considered [1–13]. Both the material and the process technology of automotive components have to fulfill ecological and economical requirements to reach more efficient components and functional units. Additionally, the improvement of at least one of the following aspects is important: increased lifetime and load capacity as well as reduced weight, friction, and lubricants. Figure 6.1 shows how the required improvements to save natural resources (both material and energy) are achievable. Therefore, surface-affecting processes, wear, fatigue, corrosion, oxidation, and friction have to be decreased.

The surface treatment of materials and surface functional optimized laminated materials are two key technologies to achieve the abovementioned challenges. Within the last decades, surface solutions based on new or improved deposition techniques, like PVD (physical vapor deposition) and PACVD (plasma-assisted chemical vapor deposition), thermochemical heat treatment, and thermal spraying were developed and industrially implemented. Figure 6.2 shows the different surface treatments with some selected main characteristics. Further details are highlighted in the following.

The described treatments become more common for power train and engine applications. Due to economical industrial implementation, traditional treatment-substrate systems (e.g., hard chromium, phosphating) are often substituted by advanced treatments. Moreover, the generating of optimized surfaces for different types of substrate materials (e.g., Al alloys, case-hardened steels, etc.) and various part geometries (e.g., bores) also

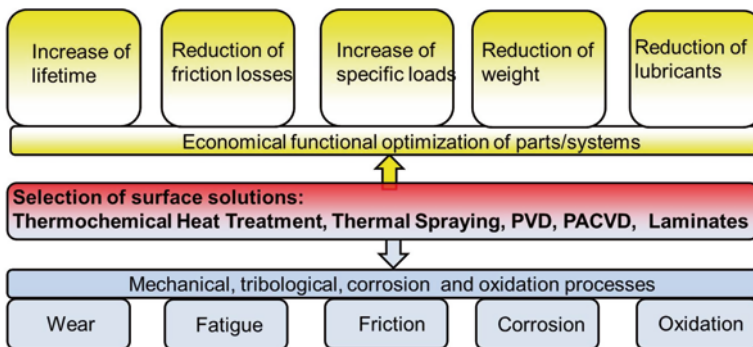


Fig. 6.1 Challenges for functional optimization of parts/systems and affecting processes including friction that have to be reduced

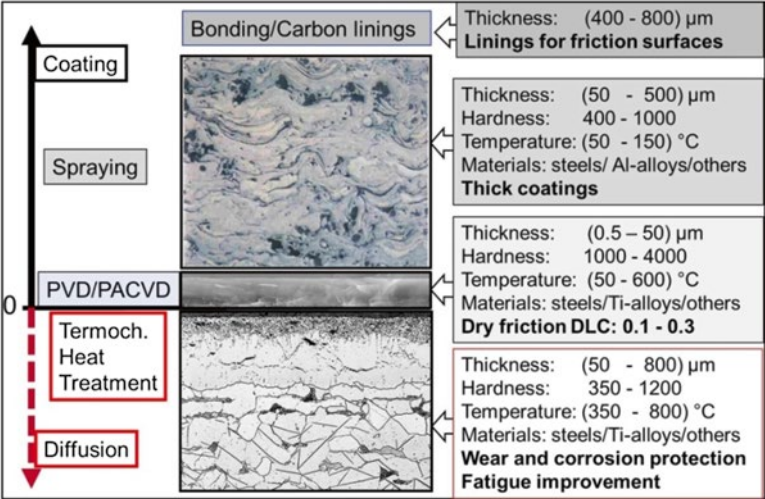


Fig. 6.2 Schematic view of surface treatments with selected main characteristics

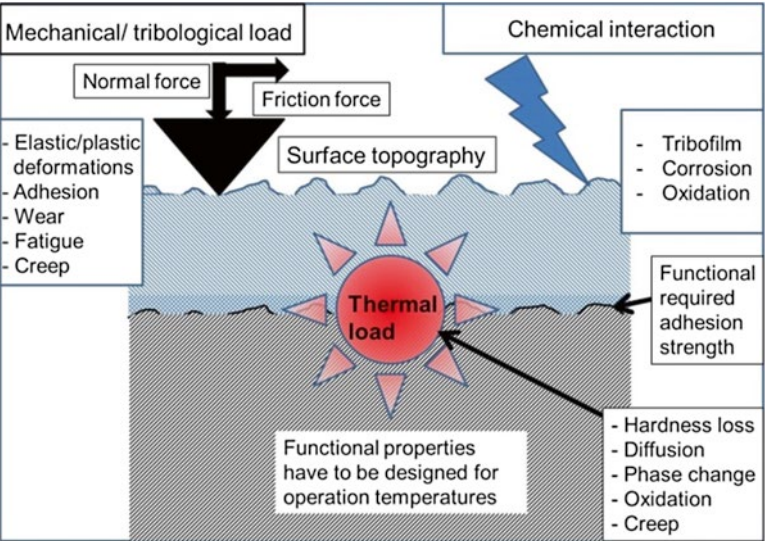
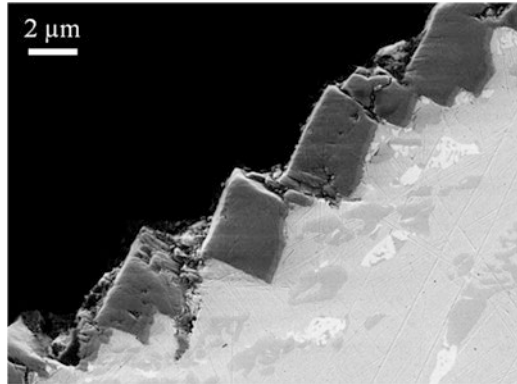


Fig. 6.3 Schematic structure of a substrate-treatment system and main surface-affecting processes at elevated temperatures

impacts the running costs; thus, often, solutions have to be selected which are a compromise between the optimal performance and the accepted manufacturing costs.

A schematic structure of a surface-treated part and the main affecting processes are shown in Fig. 6.3. A prerequisite for substrate-treatment systems is the adhesion of surface-treated areas under load conditions. It has to be pointed out that thermal load has to be taken into account. High temperature often reduces mechanical

Fig. 6.4 SEM image of a cross section of a TiAlCrN-coated valve after 100,000 cycles showing the coating failure due to thermal–mechanical overload [15]



material properties (hardness loss, etc.) and enforces the intensity of affecting processes (oxidation, etc.). Furthermore, it should be mentioned that customized surface topography by pre- and posttreatment is often a key point to fulfill functional requirements (see Sect. 6.7).

To demonstrate complex load conditions in harsh tribological systems, the load on an exhaust valve as one of the important parts in combustion engines is discussed. The valve surface is moving with high frequency resulting in impacts in the range of at least 1,000 times/s. High temperature (up to 800 °C) [14] is reached due to the hot gas having a high speed of several 100 m/s. Both mechanical (pressures up to 200 bar) and thermal stress are acting. Also, oxidizing or even corrosive components affect the surface. In extreme cases the valve surfaces are destroyed by cracking. A laboratory test of a bimetal-designed valve with a welded hard face, Stellite F, is presented to show the importance of the material selection for the base material to fit the operation conditions [15]. PVD coatings were selected to protect the valve surface. For example, TiAlCrN-coated valves were tested at a temperature of 750 °C. Figure 6.4 shows the valve-seat contacting valve surface after the test. At first it has to be noticed that the adhesion between the coating and the valve surface was sufficient. However, the coating was cracking and small parts penetrated into the substrate material. That means that the coating-substrate system showed a thermal–mechanical overload. Of course such structured hard surfaces generate high values of wear in the closed tribosystem valve-seat. This excellent example shows that both the surface treatment and the substrate material have to be optimized hand in hand.

In the following sections, both the application potential and selected industrial applied examples of different surface treatments will be shown. Mainly, plasma-enhanced surface engineering is discussed. Aspects of the internal coating of bores inside the engine by plasma spraying, features of the corrosion protection of power train parts by the IONIT OX process, and piston ring treatments are discussed in more detail.

6.2 Plasma-Assisted Surface Treatments

In the following the basics of plasma-assisted surface technology are briefly explained. Plasma-assisted surface treatments include different processes of plasma generation in terms of the used plasma, the generated coating material, and the interaction between the material flow and the substrate surface (coating) or the substrate surface near region (diffusion processes). Two plasma types are used: local thermodynamic equilibrium (LTE) plasma [16] and the thermodynamic nonequilibrium plasma (cold plasma) [17]. The local thermodynamic equilibrium plasma, short thermal plasma, is the basis for plasma spraying at atmospheric pressures. This thermal plasma melts the material used for the coating process. The plasma does not play a dominant role during coating growth itself. In contrast plasma-assisted PVD and CVD processes and plasma-assisted thermochemical heat treatment (TCHT, e.g., plasma nitriding processes) are based on cold plasmas. A cold plasma is characterized by a mixture of hot electrons and cold ions. Energized molecules, atoms, and ions are used during the coating growth or during the diffusion treatment. Table 6.1 summarizes the different plasma-assisted treatment types, the material used, and typical substrate materials.

Table 6.1 Summary of treatment types at different plasma states, used materials, and typical substrate materials (GNC gas nitrocarburizing) [1]

	Type of plasma	Material source	Surface interaction	Substrate material
Atmospheric plasma spraying	LTE plasma	Atmospheric arc discharge	Almost no plasma activity at the surface	– Metal alloys e.g., Al alloys, – Composites
Plasma-assisted TCHT	Cold plasma	Pulsed glow discharge in gas mixtures, e.g., N, H, CH ₄	– Ion impact – Surface acts as cathode – Species for diffusion are generated	– Metals, e.g., heat-treatable steels, Ti alloys
IONIT OX activation step after GNC before oxidation	Cold plasma	Pulsed glow discharge in N gas mixtures	– Ion impact – Surface acts as cathode	– Heat-treatable steels
PACVD	Cold plasma	Pulsed glow discharge in precursors, e.g., C ₂ H ₂	– Ion impact – Surface acts as cathode – Species for coating growth are generated	– Metals, e.g., bearing steels
PVD sputtering	Cold plasma	Atomizing by sputtering due to glow discharge at a target	– Ion impact – Extracted Ar ions – Sputtered atoms as growth materials	– Metals – Metal alloys – Galvanized plastics
PVD vacuum arc	Cold plasma	Evaporation by vacuum arc discharge	– Ion impact – Extracted metal ions – Evaporated atoms and ions as growth materials	– Metals – Metal alloys – Galvanized plastics

To highlight the main application areas of the different treatments, a brief description and typical application examples will be described in the following.

6.3 Thermochemical Heat Treatment (TCHT): Nitriding, Nitrocarburizing, and Oxidation

The nitriding and nitrocarburizing process is based on the diffusion of nitrogen and nitrogen plus carbon, respectively, at a temperature of about 350–600 °C mostly into ferrous materials like steel grade and cast iron, but also into Ti alloys, Al alloys, and other metallic surfaces [18–22]. Special nitriding steel grades were developed to achieve optimal nitriding results. The absorption of nitrogen and carbon creates a functional surface zone on top of the treated material. That zone can be a pure diffusion zone with a certain concentration of nitrogen. Depending on the steel grade, nitrides of alloying elements might be formed, e.g., CrN. However, a high enough nitrogen concentration at the surface (depending on the treatment type, time, and temperature, as well as steel grade) results in the formation of iron nitride phases, the γ' (gamma prime), $\gamma'-\text{Fe}_4\text{N}$, or the ϵ' (epsilon), $\epsilon-\text{Fe}_{2-3}\text{N}$. The $\epsilon-\text{Fe}_{2-3}\text{N}$ typically contains carbon. Nitrides forming the compound zone on top of the diffusion zone (thickness up 0.8 mm) with a typical thickness between 2 to 25 μm are visible as a white layer (also named white zone, compound layer) [18, 23]. As an additional step, the compound zone can be oxidized. Figure 6.5 shows schematically the architecture of steel surfaces with three types of steel modifications. The most used industrial nitriding and nitrocarburizing methods are salt bath nitriding, gas nitriding, and plasma nitriding [18]. Occasionally also, sulfur is added to the gas nitriding processes, the so-called sulfur nitriding [23–25]. In the following the plasma and gas processes for nitriding (PN, GN) and nitrocarburizing (PNC, GNC) and in addition the combination process IONIT OX (GNC/PNC/OX) will be briefly described by focusing at automotive applications.

In general the TCHT improves the surface hardness [19, 20], increases the wear resistance [26, 27], reduces the friction [26–28], improves the fatigue behavior [29–31], and increases the corrosion resistance [4, 32, 33].

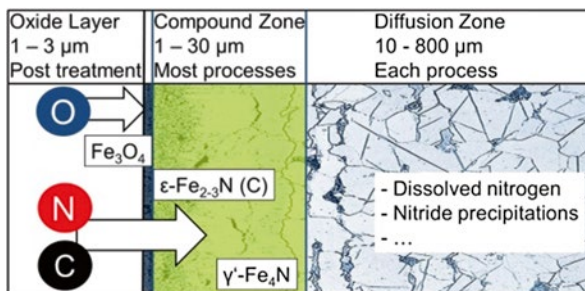


Fig. 6.5 Structure of a TCHT-treated surface with three zones; the diffusion zone is always existent; compound zone can be avoided; oxide layer is an additional posttreatment step

6.3.1 Plasma Nitriding (PN) and Plasma Nitrocarburizing (PNC)

6.3.1.1 Process Description

Plasma nitriding and nitrocarburizing are a vacuum process (mbar range in standard nitriding furnaces) for the diffusion treatment of steels, cast iron, and Ti alloys for automotive applications [20]. A glow discharge (cold plasma) is used to energize, atomize, and ionize the gas containing the diffusion elements, such as nitrogen for the plasma nitriding and nitrogen and carbon for the nitrocarburizing. The gas mixtures also mostly contain hydrogen and in some cases Ar. As a result of active nitrogen (and carbon) impinging the hot surface, they diffuse into the steel at a typical temperature of 350–600 °C. The layer is a diffusion layer with a certain concentration of nitrogen in the hydrogen/nitrogen gas mixture. However, also the γ' (gamma prime)- or ϵ' (epsilon)-type compound layers can be generated. Compared to the salt bath nitriding, GN, and GNC, the easy control of the compound zone growth is an advantage. The nitriding processes for automotive parts are mostly carried out in hot-wall furnace plasma nitriding systems as shown in Fig. 6.6.

For the evacuation of plasma nitriding systems, rotary vane and Roots blower pumps are used to achieve a vacuum state. Hot-wall furnaces operate with different heating elements for the heating of the parts and are combined with air cooling ventilation. In this way it is possible to achieve a certain degree of separating thermal and chemical processes. The negative voltage of the glow discharge is applied to the loaded parts. Regular pulsed power supplies are used with pulse frequencies in the range of several kHz to several 10 kHz. Gas bottles are usually used for the gas supply since the gas consumption rate is very small (liters/hour). The temperature is measured directly on at least one part of the load to control the treatment temperature. The external heating and cooling system controls the load temperature.

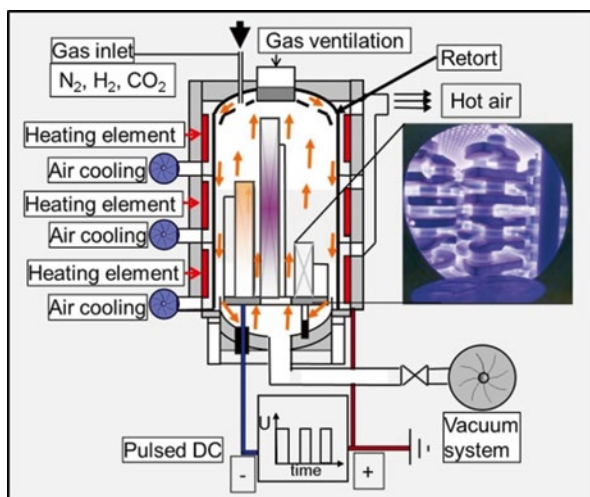


Fig. 6.6 Schematic view of a hot-wall furnace plasma nitriding system

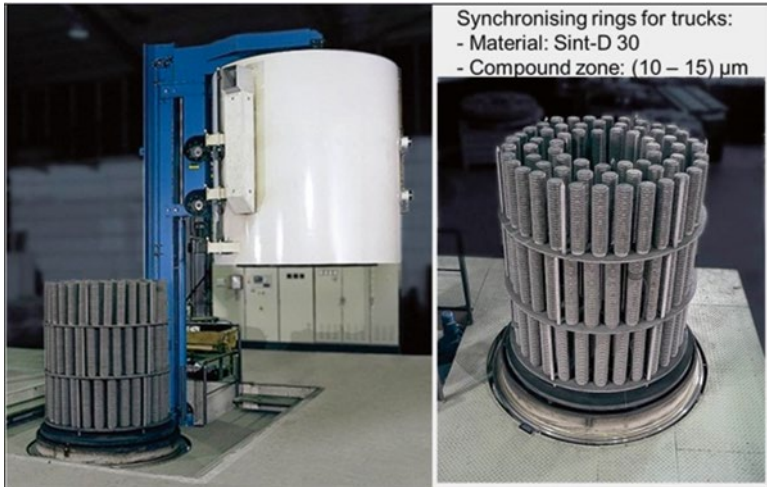


Fig. 6.7 Dual bell furnace plasma nitriding system and a charge of treated synchronizer rings made of sintered steel (courtesy of Oerlikon Metaplas)

Table 6.2 Characteristics of plasma-nitrided steels

Material type	AISI/SAE	DIN	Surface hardness HV 2	Nitride hardness depth (mm)	Compound layer thickness (µm)
Structural	1020	1.0037	150–350	0.3–0.8	4–10
Carbon	1045	1.0503	350–500	0.3–0.8	4–15
Case hardened	5115	1.7131	550–700	0.3–0.7	6–10
Heat treatable	4140	1.7225	550–650	0.2–0.6	4–8
Nitriding	A355	1.8550	900–1,100	0.2–0.5	2–10
Hot work	H13	1.2344	900–1,200	0.1–0.3	2–10
Cold work	D2	1.2379	900–1,250	0.1–0.2	–
High speed	M2	1.3343	1,000–1,250	0.005–0.1	–
Stainless	316	1.4571	950–1,250	0.05–0.1	–

Figure 6.7 shows a typical dual bell plasma nitriding system with a charge of treated synchronizer rings made of sintered steel. The advantage of a dual bell system compared to a single bell system is the higher productivity due to the additional cooling station.

6.3.1.2 Selected Properties of Treated Steel Surfaces

Plasma nitriding and nitrocarburizing can be applied on all steel grades, cast iron, and sintered steels. Typical characteristics for some treated steels are shown in Table 6.2.

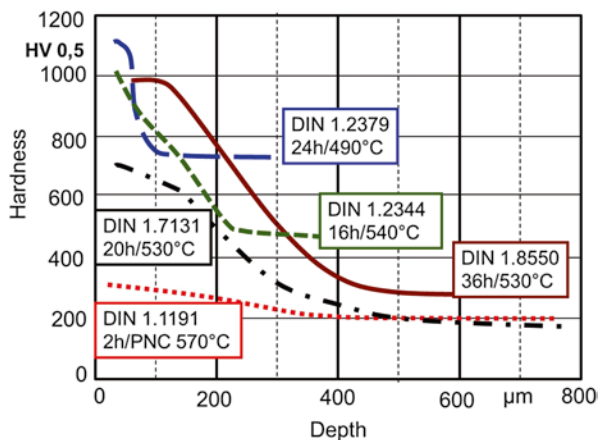


Fig. 6.8 Hardness versus depth for different plasma-nitrided steel grades

The achievable surface hardness increases with the content of metallic alloy elements (Cr and others) which are able to form nitrides. A compound zone is not formed at high-alloyed steels (e.g., HSS, AISI 316). Figure 6.8 shows typical hardness curves versus depth for different plasma-nitrided steel grades.

Typical steel grades treated by PN and PNC for automotive applications are carbon steels (e.g., AISI 1045, DIN 1.1191), case-hardened steels (e.g., AISI 5115, DIN 1.7131), heat-treatable steels (e.g., AISI 4140, DIN 1.7225), and nitriding steels (e.g., AISI A355, DIN 1.8550). Also, the special treatment of sintered steels (e.g., DIN Sint D30) is possible with a PN and PNC process. The corrosion resistance of plasma-nitrocarburized surfaces can be increased by a post-oxidation process.

6.3.1.3 Selected Automotive Applications

The treatment of clutch components such as lamellas, bells, and synchronizers is the main automotive application for PN and PNC. Figure 6.9 shows selected clutch components including the special application for synchronizers made of sintered steel. Further applications for combustion engines are sleeves for heavy diesel engines, tappets, crankshafts, camshafts, and piston heads. There is also a high potential to treat gears for transmission applications.

6.3.2 Gas Nitriding (GN) and Gas Nitrocarburizing (GNC)

6.3.2.1 Process Description

The gas nitriding process, also called ferritic gas nitriding, is based on nitrogen diffusion usually by the use of ammonia with or without atmosphere dilution. Steel components are mostly heated to a temperature of 500–520 °C. The ammonia is

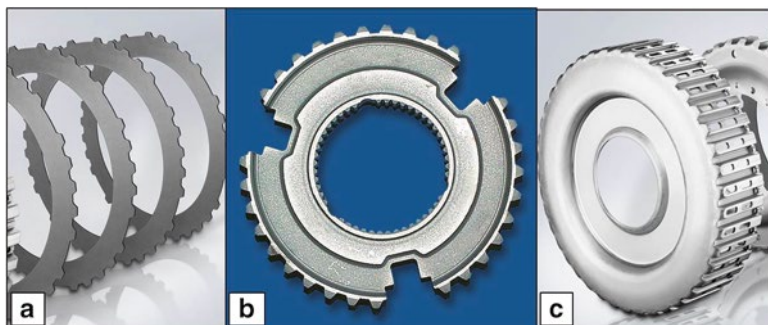


Fig. 6.9 PN- and PNC-treated clutch parts, (a) synchronizer lamellas, (b) sintered steel synchronizer, and (c) clutch bell (courtesy of Oerlikon Metaplas)

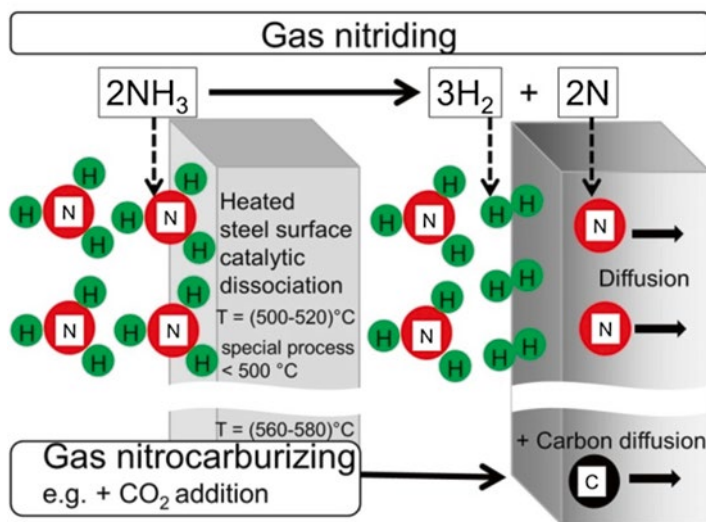


Fig. 6.10 Schematic description of the gas nitriding and gas nitrocarburizing process

dissociated due to the temperature and the catalytic effect of the steel surface [18, 19, 34–36]. A special process operates at temperatures lower than 500°C to treat spring steels [37]. The principle of the gas nitriding process is shown in Fig. 6.10.

The ammonia dissociates into atomic nitrogen and hydrogen as shown in Eq. 6.1:



The instable atomic nitrogen is immediately combining to form molecular nitrogen according Eq. 6.2:



As long as nitrogen exists in an atomic state, it is absorbed at the steel surface. The following chemical reaction is shown in Eq. 6.3:



Nitrogen diffuses into the steel. Hydrogen stays in the gas atmosphere. The degree of nitrogen diffusion is determined by the temperature and the amount of nitrogen that can penetrate and diffuse into and away from the surface in accordance to the diffusion law. Also, the steel grades, especially the alloying elements, and the outer layer of the steel (machined surface, contamination) play an important role too.

Gas nitrocarburizing is characterized by the addition of a carbon-containing gas at higher temperatures of 560–580 °C. Common carbon-containing gases are CO_2 , C_3H_8 , and special gas mixtures (exogas, endogas). After nitriding or nitrocarburizing, an oxidation step can follow using gases or gas mixtures containing oxygen, air, N_2O , or water [38].

6.3.2.2 Selected Properties of Treated Steel Surfaces

The primary objective of GN and GNC is to improve the wear resistance combined with friction reduction. This is achieved by the compound zone (white layer) at the surface of the part. In the first approximation, the same hardness depth characteristics are obtained underneath the compound zone as for PN and PNC processes (see Fig. 6.8). It has to be noticed that the thick compound layer shows an open porosity [19]. Figure 6.11 shows a typical hardness distribution of a compound zone consisting of a dense (in direction to the core) and a porous zone (in direction to the surface) [40]. A thick ϵ -compound zone is preferred for several applications, e.g., for corrosion protection if a post-oxidation is added (see Sect. 6.3.3).

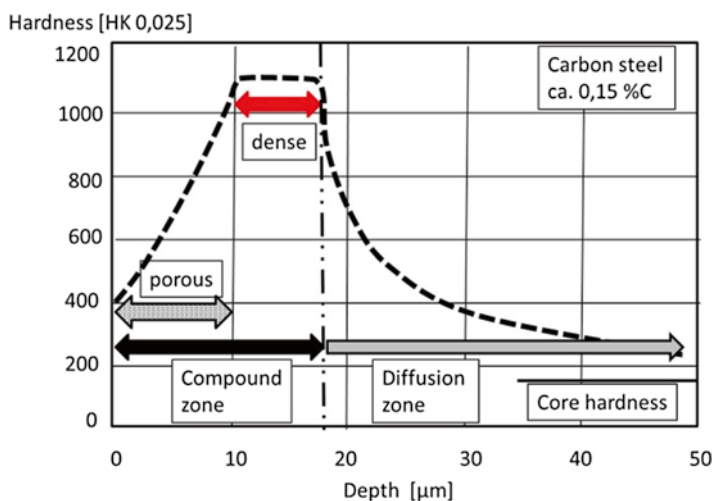


Fig. 6.11 Hardness versus depth for a thick compound zone with increasing porosity in direction to the surface [39]

Fig. 6.12 Springs treated by the low-temperature GN process (METANIT) (courtesy of Oerlikon Metaplas)



6.3.2.3 Selected Automotive Applications

The application field of GN and GNC is similar to the above description of PN and PNC. It is also similar for that of IONIT OX process described under Sect. 6.3.3. It shall be mentioned that almost all piston rings are treated by gas process.

One special GN process is the METANIT process. It is operated at a temperature below 500 °C. Materials commonly used for springs and dampers will lose their specific properties when treating them with temperatures higher than 450 °C. Applying this low-temperature process, it is possible to increase the fatigue limit of springs by an additional 30 % due to the surface stress. That process is used in mass production for valve springs as well as for other springs (disk, clutch) and torsion dampers. Examples of treated springs are shown in Fig. 6.12.

6.3.3 The IONIT OX Process

6.3.3.1 Process Description

Automotive and hydraulic parts often require a combination of good corrosion resistance, low friction properties, wear resistance, and good surface hardness in addition. To achieve these surface requirements, a complex process, the IONIT OX process, was developed by Sulzer Metaplas [4, 40]. It combines gas nitrocarburizing and plasma activation with a controlled oxidation process. Figure 6.13 shows the process sequences in detail. The treatment is divided into the following phases: heating, gas nitrocarburizing, intermediate cooling, evacuation, plasma activation, oxidation, and cooling.

Figure 6.14 shows a schematic system setup. All components used for gas processes and plasma processes are combined and added with components allowing the oxidation step. The systems can operate as pure PN or PNC systems or as pure

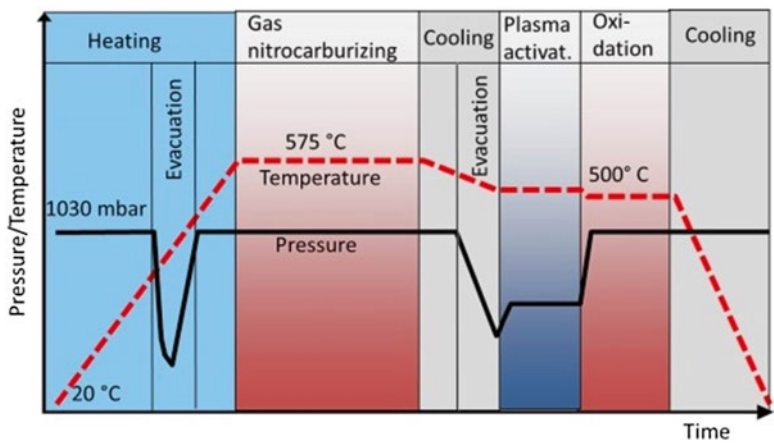


Fig. 6.13 The IONIT OX process: combination of plasma-supported vacuum process with normal pressure process in one cycle

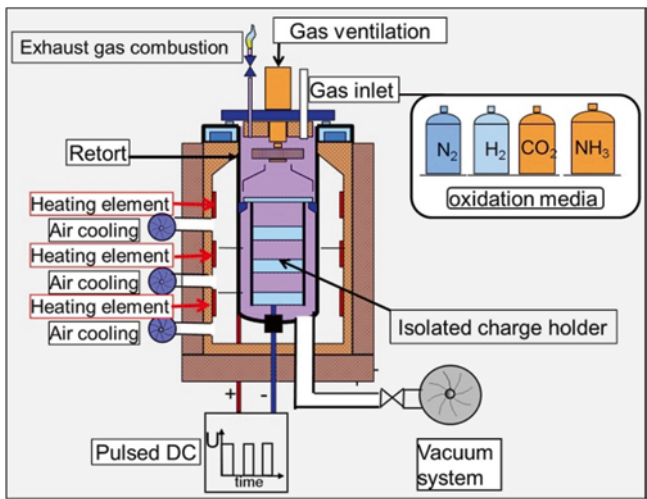


Fig. 6.14 Schema of an IONIT OX system combining gas, plasma processes, and oxidation

GN or GNC systems. Figure 6.15 shows a schematic view of an IONIT OX furnace and charge holder for ball pins.

During the gas nitrocarburizing step, both a diffusion zone and a compound zone are created. The controlled growth of a pure ϵ -compound zone produces a defined pore structure. Plasma activation causes the modification of the compound zone top surface. This produces a very clean surface having a numerous nuclei on which an extra-fine, dense oxide layer grows. In the oxidation step, the strongly adhering 2–3 μm thick layer is created on the surface of the modified compound zone.

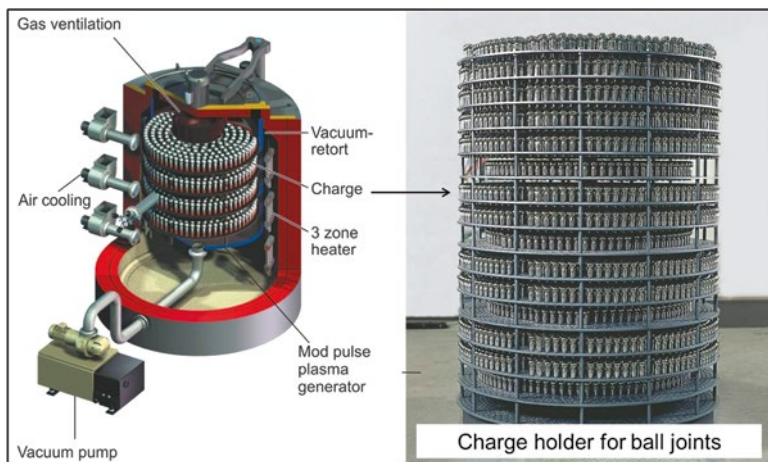


Fig. 6.15 Schematic view of an IONIT OX furnace and charge holder for ball pins [20]

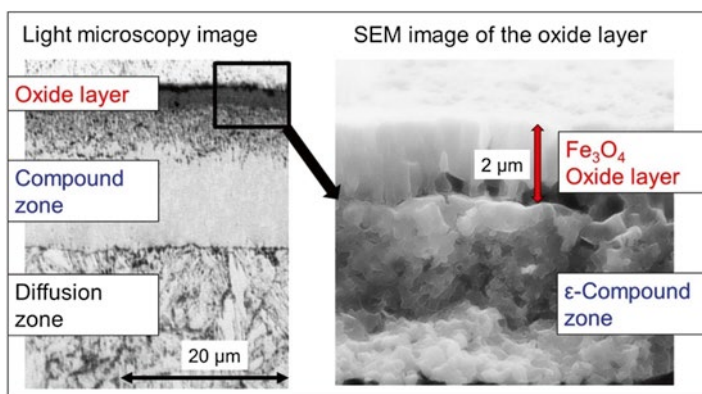


Fig. 6.16 Microstructure of an IONIT OX-treated steel showing three distinct zones [20]

The strong bonding is achieved due to the very good interlocking characteristics between the oxide and the porous compound zone.

A light microscopy and SEM image of a typical microstructure of IONIT OX-treated steel consisting of three distinct zones is shown in Fig. 6.16.

The SEM image of the oxide layer microstructure shows that the Fe_3O_4 layer crystallizes in a double-zone layer structure. While the inner zone has a fine crystalline structure, the outside zone has a palisade structure. It is assumed that the pore area of the nitride layer, which is included in the growth of the oxide layer, improves the formation of the oxide to a fine oxide structure and increases the related thickness. This model shows that the inner zone grows by nitride decomposition, while the outer zone grows by iron oxide formation [4].

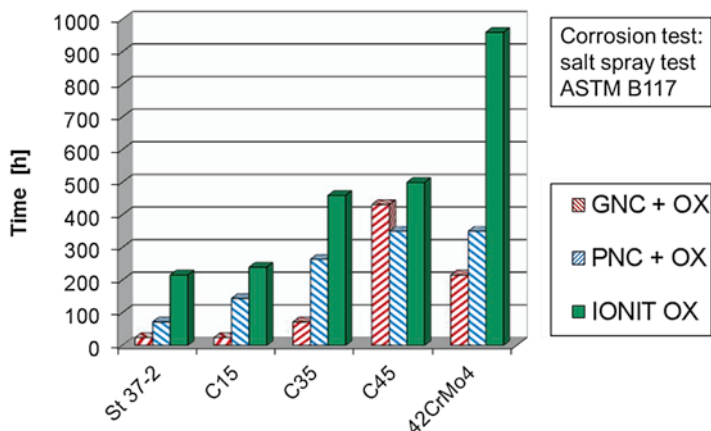


Fig. 6.17 Salt spray test results of IONIT OX-treated steel surfaces in comparison to gas nitrocarburizing with oxidation (GNC+OX) and plasma nitrocarburizing with oxidation (PNC+OX) [40]

6.3.3.2 Selected Properties of Treated Steel Surfaces

Figure 6.17 shows the significant corrosion resistance improvement of steels by an IONIT OX treatment in comparison to gas and plasma nitrocarburizing with post-oxidation. In salt spray tests (DIN 50 021 SS, according to ASTM B117), IONIT OX-treated C35 (AISI 1035), C45 (AISI 1045), and 42CrMo 4 (AISI 4140) parts remain free of signs for corrosion for more than 400 h compared to plasma-nitrocarburized and plasma-oxidized C35 parts that could reach 260 h and 42 CrMo4 parts that could reach 320 h [40].

One of the reasons for the high corrosion protection of IONIT OX-treated steels is the dense layer structure of the Fe_3O_4 oxide. The reason for decreased corrosion resistance for base material with low carbon concentration could be explained with a decreasing of the pure ϵ (epsilon)-type compound zone to a more γ' (gamma prime)-containing compound zone.

It has to be mentioned that salt spray tests demonstrated that the IONIT OX treatment is often superior to classical treatments such as salt bath nitrocarburizing with post-oxidation and even in comparison to standard hard chromium or chemical nickel-plated surfaces [20, 41].

6.3.3.3 Selected Automotive Applications

IONIT OX-treated automotive parts include ball pins, pivot spindles for timing bells, piston rods, guide pins, gear selector shafts, plungers of gas-pressure springs, pinion shafts, wiper spindles, wiper blade holders, and pump cases. Selected parts are shown in Fig. 6.18.

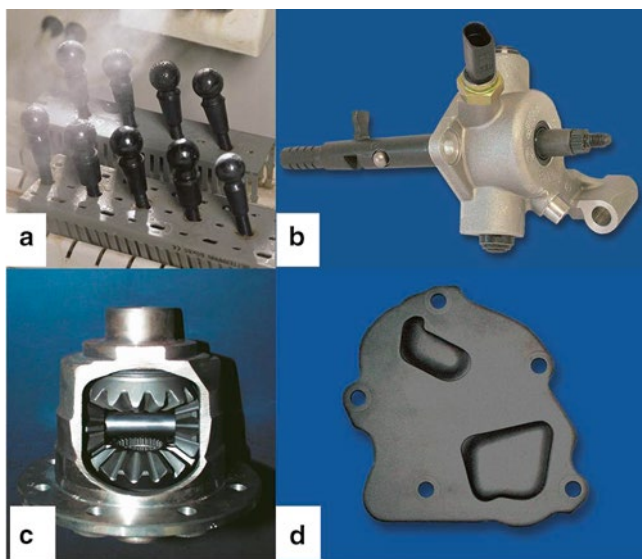


Fig. 6.18 Selected applications of IONIT OX-treated automotive parts: (a) ball pins, (b) gear selector shaft, (c) pinion shaft, and (d) pump case

The surface treatment meets complex ball pin performance requirements. For instance, ball pins have to guarantee resistance to both general and fretting corrosion. Additionally, a low friction momentum of the system ball against plastic cup and locker ring, as well as stability against abrasive particles intruding into the ball pins, is required. The treated balls meet salt spray test requirements of 240 h minimum without any signs of red rust.

6.4 PVD Processes

PVD deposition processes are applied to coat automotive parts with hard coatings for wear and friction reduction with a coating thickness range of 0.5–50 μm [41–44]. Both classical hard coatings (nitrides, carbonitrides, and oxynitrides) and DLC coatings are deposited. The hardness of the coatings covers a range of 10–50 GPa. The process temperature is in the range of 200–500 $^{\circ}\text{C}$. The two most common deposition methods are the cathodic vacuum arc evaporation (CVAE), dominating in application with classical hard coatings, and magnetron sputtering (MS), mostly used for DLC coatings. Hydrogen-free DLC coating of the ta-C type is only deposited by CVAE [45]. Both processes are plasma processes running under vacuum condition in the pressure range of about 0.01–10 Pa.

6.4.1 Cathodic Vacuum Arc Evaporation (CVAE)

6.4.1.1 Process Description

The CVAE process starts under high vacuum conditions (or with a low-pressure gas atmosphere) by triggering an arc plasma discharge between a conducting solid cathode and an anode. The evaporation current can be typically DC 50–200 A, pulsed at several kA, or even superimposed DC and pulsed current. Typical operating voltages of the arc discharge are in the range of 15–50 V for DC arc discharges. The evaporated material consists of energized atoms and positive ions having a high kinetic energy (several 10s of eV) and droplets of the cathode material often called “macroparticles.” The total ionization fraction of the evaporated atomized material reaches extremely high values of 50 up to 100 % [45, 46]. Reactive gases nitrogen-, carbon-, and also oxygen-containing gases are used to deposit MeN, MeNC, and MeNO coatings with different contents of N, O, and C. The parts are heated to temperature between 200 and 500 °C. Furthermore, the parts are ion cleaned before the coating deposition process starts. The parts have a negative bias during the coating growth.

A schematic view at a cross section of a circular or rectangular simple constructed arc evaporator is shown in Fig. 6.19. The arc cathode is mounted at a cooling plate. Mostly, a magnetic field is applied to steer and/or to confine the arc movement. Often, the arc is triggered by a mechanical trigger making an electrical shortcut which is fast opened; thus, a triggering plasma cloud is generated.

Besides, circular and rectangular evaporators and also evaporators with tubular arc cathodes are in use [46].

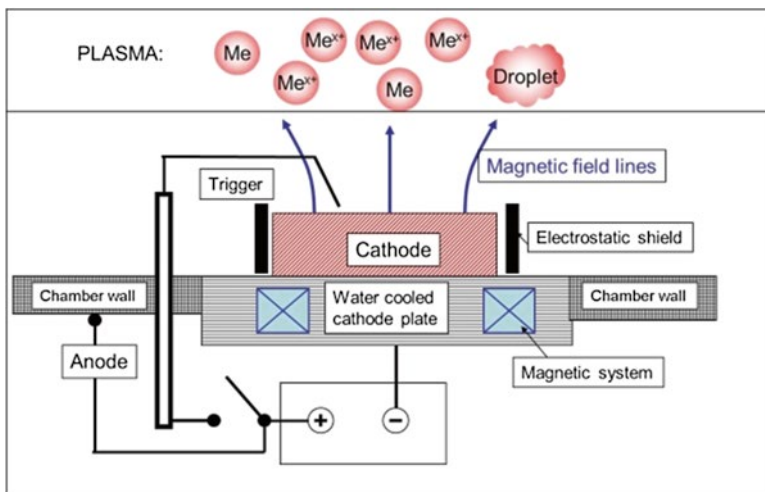


Fig. 6.19 Schematic view of a typical arc evaporator

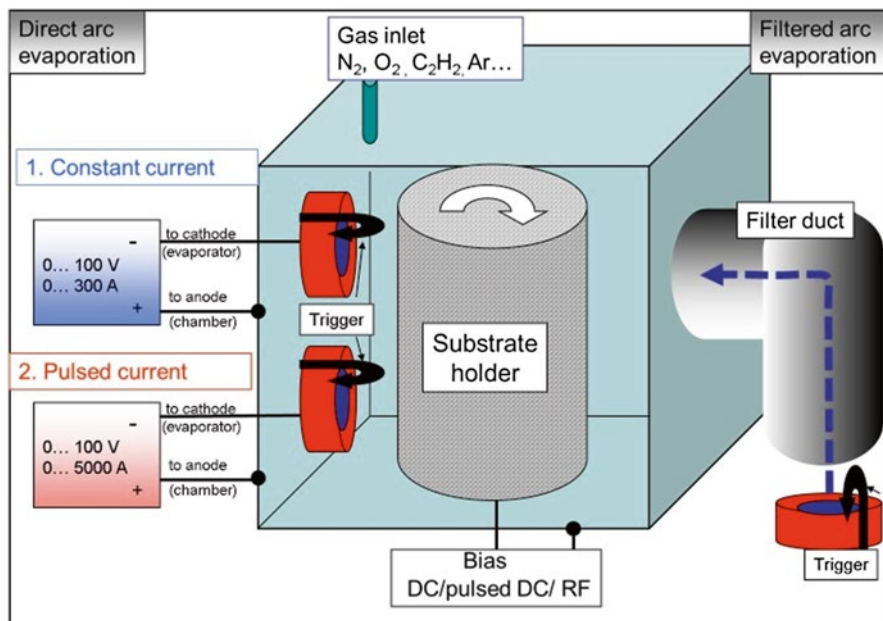


Fig. 6.20 Operation modes of arc evaporators, direct arc with constant and pulsed current, and filtered arc

Two different industrially applied arc deposition processes are shown in Fig. 6.20:

- (a) Direct cathodic vacuum arc evaporation (DCVAE):
constant current or pulsed arc discharges with no means to separate the plasma flux from the macroparticles. The coating contains several droplets.
- (b) Filtered cathodic vacuum arc evaporation (FCVAE):
constant current or pulsed arc discharges using some means to separate the directions of the plasma flux and the macroparticle flux, so that only the plasma is directed to the substrate surfaces resulting in nearly droplet-free coatings.

For automotive applications, the DCVAE is dominating. DLC coatings of the type ta-C are deposited also by FCVAE.

Figure 6.21 shows an industrial batch PVD system equipped with arc evaporators for automotive components. The chamber has four flanges each equipped with eight circular evaporators of a diameter of 100 mm. The coating zone is about 1,400 mm in height and 1,200 mm in diameter. The ion cleaning is done either by AEGD (arc-enhanced glow discharge) [47] or metal ion bombardment. The growth rate at twofold rotation is up to 5 $\mu\text{m/h}$.

CrNO coatings are deposited by adding oxygen to the nitrogen. The processes for coatings with a thickness of up to 50 μm are implemented.

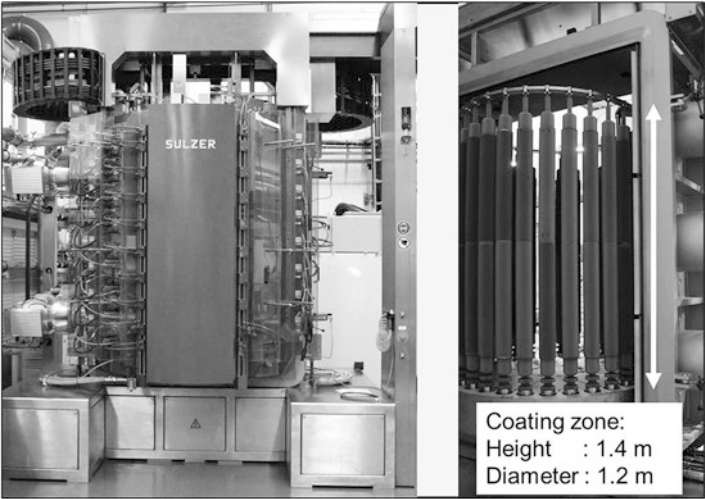


Fig. 6.21 Large CVAE batch system for automotive components equipped with a substrate holder for piston rings (courtesy of Oerlikon Metaplas)

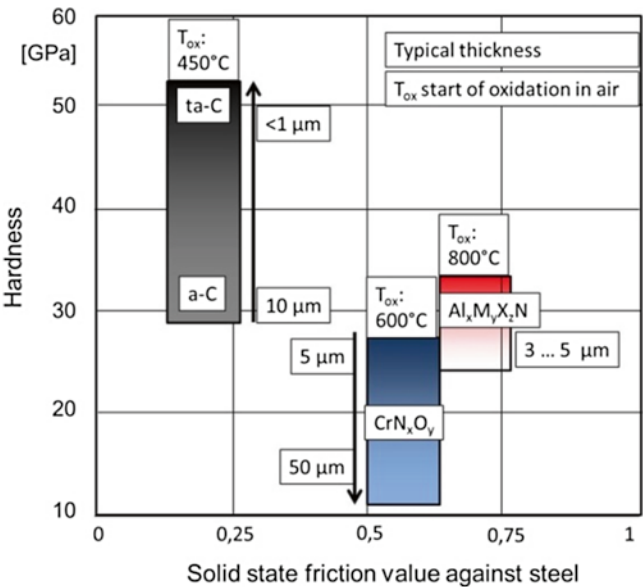


Fig. 6.22 Main coating types deposited by CVAE used for automotive applications

6.4.1.2 Selected Coating Properties

Figure 6.22 shows the currently main coating types deposited by CVAE for automotive applications. The hardest coating is the ta-C coating, also having the lowest friction value against steel in dry friction conditions [48]. Mostly, Cr-based coatings of the

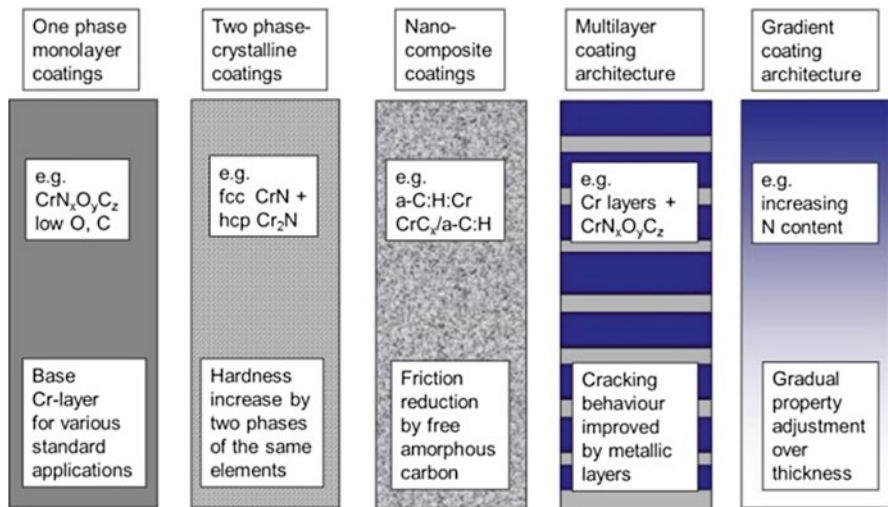


Fig. 6.23 Coating types and architectures within one base coating type in use: example $\text{CrN}_x\text{O}_y\text{C}_z$

type $\text{CrN}_x\text{O}_y\text{C}_z$ with different ratios x , y , z are applied to different components [49]. Detailed coating architectures for industrial use are mostly not available due to know-how protection of the companies. Different possible coating structures and architectures are highlighted in Fig. 6.23. Homogeneous monolayers and two-phase crystalline layers are often part of a multilayer coating or gradient coating. The simplest coating might be a Cr bonding layer (some 100 nm thick) followed by a more or less stoichiometric CrN. If higher temperatures are stressing the component surfaces, e.g., turbo charger components, then coatings which show higher oxidation stability than CrN are necessary. This is true for AlMeN-based (Me as a metal or metal alloy) coating. AlTiN- and AlCrN-based coatings show a higher oxidation stability [50, 51]. Coatings of the type MeSiN like TiSiN show relevant properties for high temperature applications.

6.4.1.3 Selected Automotive Applications

Figure 6.24 shows selected arc PVD-coated automotive parts both applied with Cr-based coatings and hydrogen-free DLC. The main application for Cr-based coatings with different architectures is piston rings [52]; thin ta-C-based coatings are mainly deposited on tappets [7]. Selectively also, camshaft drive system parts are coated by CrN coatings. Valves are coated mostly only for racing applications [53]. A newer development is the PVD coating of timing pin bolts [54]. The coating technology has so far not been described by the manufacturer. Anyhow, CVAE has high potential for that application.

In the following some selected applications are highlighted in more detail.

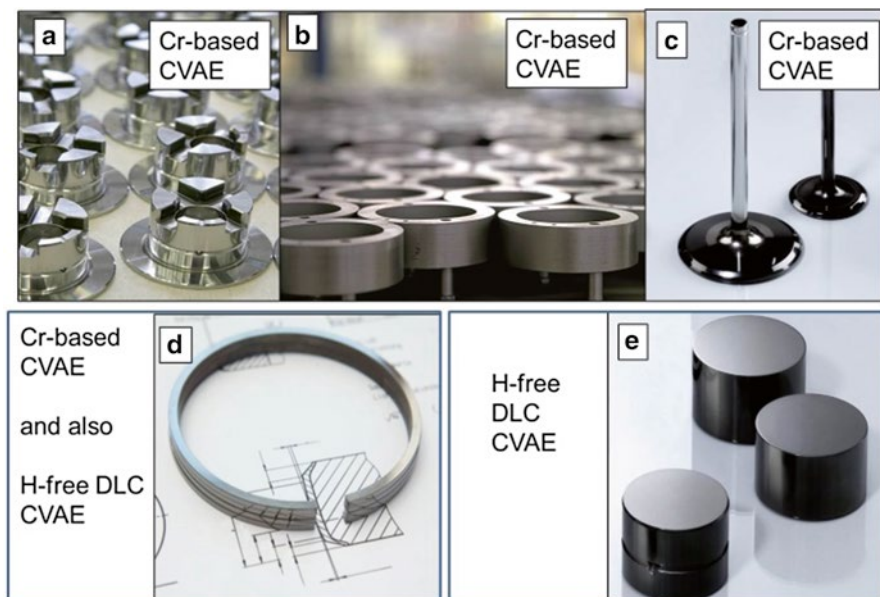


Fig. 6.24 Selected arc PVD Cr-based coatings and hydrogen-free DLC-coated automotive parts: (a) camshaft drive components (courtesy of Oerlikon Metaplas), (b) pump housing for diesel pumps (courtesy of Oerlikon Metaplas), (c) valves, (d) piston rings (courtesy of Federal-Mogul), and (e) tappets [7]

Piston Rings: Reduction of Wear and Scuffing

Piston rings seal the combustion gas and control the lubrication oil transport. The surface treatment is used to reduce wear and to prevent scuffing. Besides the different substrate materials (steel grades, gray cast iron), also different surface treatments are used. Figure 6.25 shows different surface treatments developed and/or applied over the past 30 years.

Depending on the application and the manufacturing costs, nitriding, spraying, galvanizing, PVD and PACVD coatings, and the combination nitriding plus PVD coating (see also Sect. 6.6) are used. It is interesting to mention that the first industrial applied component coating for combustion engines is the deposition of MoN on piston rings at the end of the 1970s by CVAE [55]. About 10–50 μm thick Cr-based PVD coatings with different chemical compositions and architectures are deposited mostly by CVAE evaporation. Cross section (SEM and light microscope) images of a CrNO coating deposited by CVAE are shown in Fig. 6.26.

There is a permanent development of new coating materials for piston rings, e.g., AlTiN in combination with CrN [56]. Recently, it was reported that also hydrogen-free DLC coatings deposited by CVAE are applied for piston rings [57]. That DLC coating type combines high wear resistance with very low scuffing tendency.

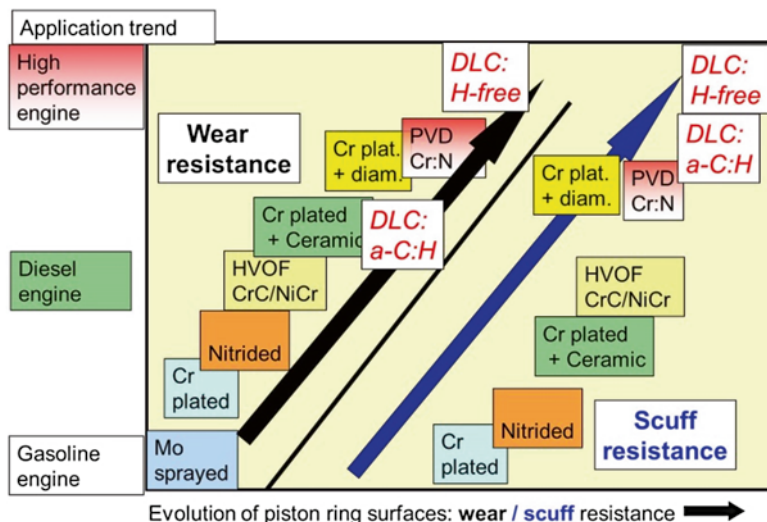


Fig. 6.25 Different piston ring treatments and the estimated wear increase and scuffing resistance. *HVOF* high-velocity oxygen fuel spray, *Cr plat. + diam.* Cr plated + diamond

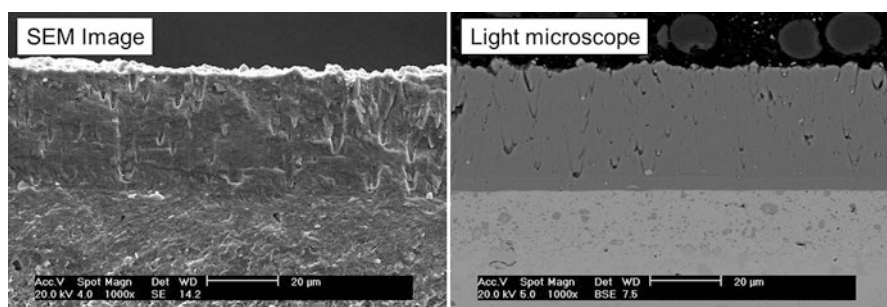


Fig. 6.26 SEM and light microscope cross section image of a typical CrNO coating for piston rings deposited by CVAE [49]

Drive Components and Pump Housing

Parts of the camshaft drive system like bearing journals, guide sleeves, and thrust and axial bearing washers are partially coated by CrN to reduce the wear of a timing pinion setup. Pump housings of diesel pumps for heavy-duty applications are coated on the inner side to reduce wear caused by abrasive particles in the diesel.

Valves

At the present time, the coating of valves is limited mostly on high-loaded engines like racing application. Ti alloys are coated with CrN [53].

Tappets: ta-C

It was shown that ta-C coatings with a thickness of less than 1 μm , approx. 500 nm, are able to reduce wear and friction in the valve system if tappets are coated. That solution was introduced by Nissan. The reduction of friction based on the combination of coating and a special developed lubricant [7].

6.4.2 Magnetron Sputtering (MS)

6.4.2.1 Process Description

The magnetron sputtering process is based on the atomization of coating material by means of a momentum transfer mechanism [41–43, 58]. Figure 6.27 shows a schematic drawing of a magnetron sputter source. A magnetic field (strength several 10 mT) is applied to the cooled target. Ar is added into the deposition chamber (pressure 0.1–1 Pa). A high negative voltage is applied to the target (300–1,000 V). The glow discharge ionizes the Ar atoms. The kinetic energy attained by the ions is transferred to the target material upon impact. As a result atoms from the target surface are atomized. The ionization degree of the sputtered material is rather low in comparison to the arc discharge (several percent only) [59]. Different magnetic field setups are in use, the balanced magnetron (BM) and the unbalanced magnetron (UBM) [60]. Mostly, rectangular magnetron sources are in use, for certain application also tubular ones, as will be shown below. The magnetron discharges are operating mostly in DC or pulsed DC. A newer method is the HiPIMS discharge (high power impulse magnetron sputtering) enabling a significant increase of the ionization of the sputtered target material [59]. Reactive gases are added to

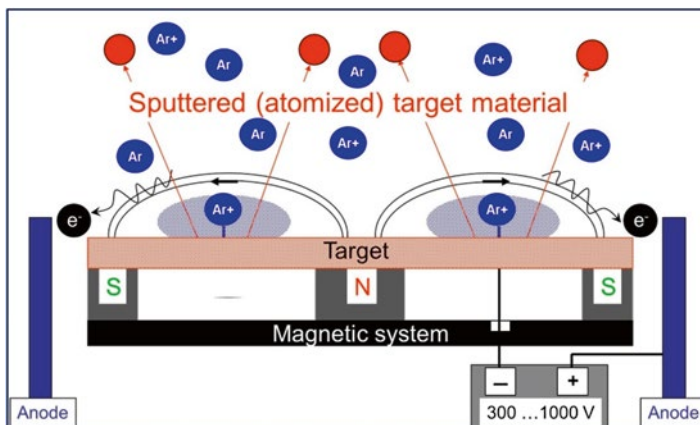


Fig. 6.27 Schematic drawing of a typical magnetron sputter source

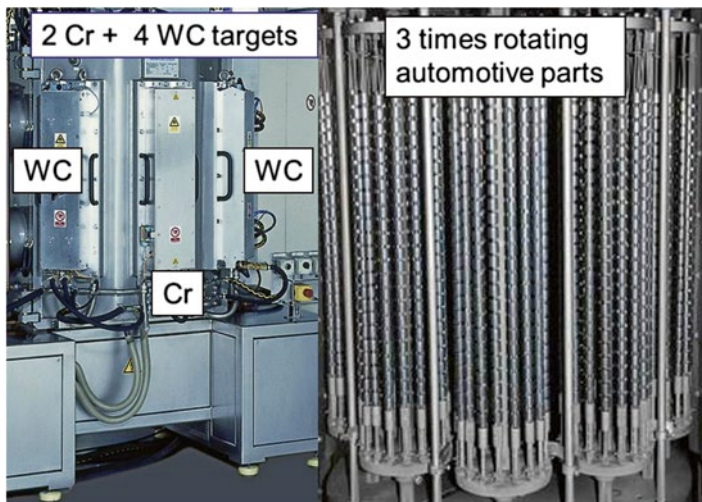


Fig. 6.28 Sputter system with six rectangular magnetrons. *Left* closed chamber, *right* open chamber, and *mid* substrate holder for three-time rotation loaded with automotive parts coated with a-C:H:Me coatings (courtesy of Oerlikon Metaplas)

the Ar working gas to deposit hard coatings, e.g., nitrogen for CrN. A bias voltage is added to the substrate. The parts are heated in the range of 200–500 °C. An ion cleaning of the parts before the deposition of a hard coating is done.

Sputtering can be applied for the same applications like the abovementioned CVAE, e.g., Cr-based coatings on piston rings. It should be mentioned that the achievable growth rates are lower than that of the arc process; thus, the magnetron is not widely used for classical hard coatings. Magnetron sputtering is dominating in DLC applications for automotive parts excluding the above-described ta-C coating [61]. Figure 6.28 shows a coating unit equipped with six rectangular magnetron sources. In each case three sources in the two doors of the octagonal chamber are suitable to deposit both Cr-based coatings and DLC of the type a-C:H:Me. In the same sputtering equipment, also PACVD processes are carried out to deposit a-C:H and a-C:H:X coatings (see Sect. 6.7). For the deposition of DLC coatings, low temperatures with values mostly around 200 °C are chosen.

6.4.2.2 Selected Coating Properties

In the following a concentration on the deposition of DLC coatings by the sputtering process is made because it is the main industrial application. Figure 6.29 shows the usage of metallic, carbide, and graphite targets to deposit complex coating architecture consisting often of three parts: bonding layer, support layer, and DLC top layer.

The sputtering process is the standard method to deposit bonding layers and support layers for various functional DLC top layers. If graphite targets are used to deposit the functional DLC top layer, by adding a carbon-containing gas (e.g., C₂H₂),

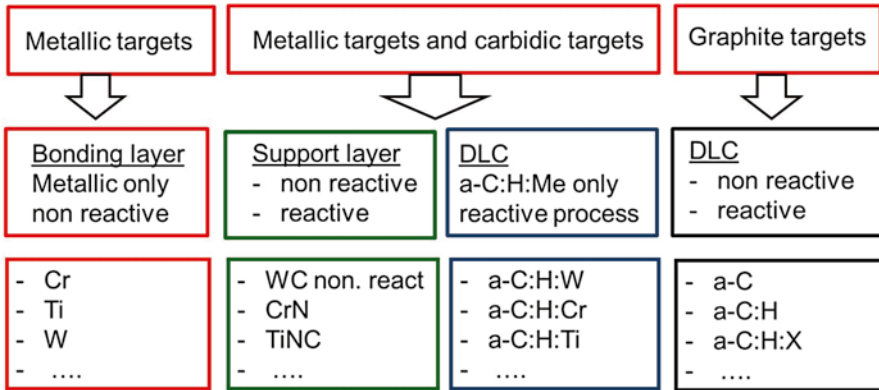


Fig. 6.29 Usage of metallic, carbide, and graphite targets to deposit complex coating DLC architectures

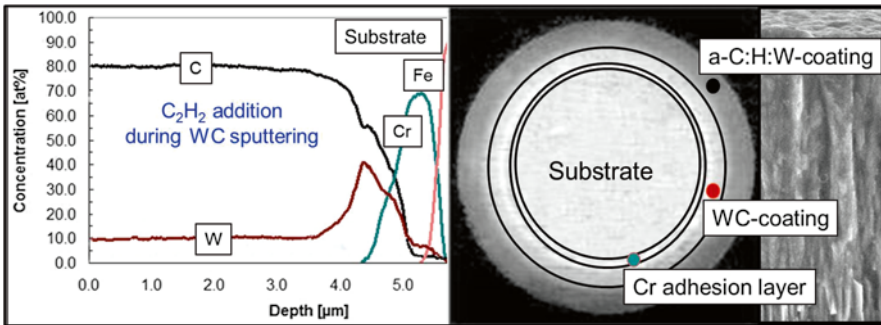


Fig. 6.30 Chemical depth profile, calotte, and SEM micrograph of an a-C:H:W coating architecture

then metal-free a-C:H coatings are generated. The historically first sputtered DLC coating for automotive applications was the a-C:H:W coating for the Volkswagen unit injection system [62].

Figure 6.30 shows the typical coating architecture of an a-C:H:W coating consisting of a Cr bonding layer (Cr target), nonreactive sputtered WC support layer (WC target), and functional DLC layer deposited by adding C_2H_2 to the Ar sputtering gas (WC target). The depth profiling of the chemical composition (without hydrogen) measured by SIMS is shown additionally.

The typical hardness range is between 10 and 15 GPa. This coating type offers the highest toughness of all DLC types and shows excellent running-in characteristics that are demonstrated in Fig. 6.31. The originally rough surface of the tested part for the engine management was smoothed without destroying the coating. After a longtime test, only some wear appearing as polishing effect is visible.

Besides the traditional a-C:H:W coatings, also a-C:H:Cr coatings are in discussion to be used in tribosystems lubricated with a high MoDTC addition [63].

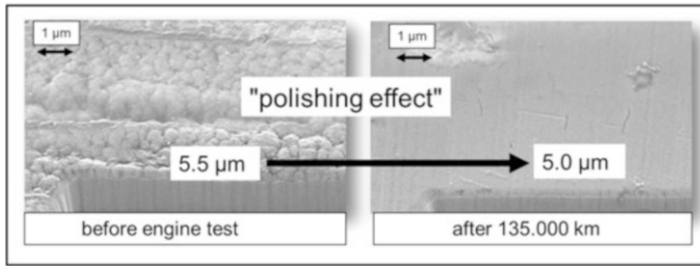


Fig. 6.31 FIB–SEM images of the topography of an a-C:H:W-coated part for the engine management before use and after 135,000 km

Fig. 6.32 Starter gear coated with a-C:H:W for reduction of the starting power (source: Oerlikon Metaplas)



6.4.2.3 Selected Coating Applications

The functional top coating of the type a-C:H:Me as the first DLC coating type introduced by Volkswagen for passenger cars is still used in selected automotive applications; however, that coating type is more and more substituted by coating systems having an a-C:H or a-C:H:X functional top coating (see Sect. 6.6). One of the main common uses of a-C:H:Me coatings is the deposition as a support layer for the a-C:H or a-C:H:X functional top coating. Nevertheless, there are still some a-C:H:Me applications for the same parts which are described in Sect. 6.6 as applications for PACVD-deposited functional top coatings, especially for piston rings.

It was shown that a-C:H:Me coatings have great potential to be coated on gears to decrease pitting formation, to minimize the required lubrication (additives), and/or to increase the specific loads [1]. However, for automotive power train components, it is not utilized in industrial practice. The costs for a DLC coating might be one of the reasons for that. Figure 6.32 shows a gear application for motorcycles. The gear coating with a-C:H:Me reduced the required electrical current for starting by a factor of about two.

6.5 PACVD Process for DLC Coatings

The PACVD (plasma-assisted chemical vapor deposition) process for automotive applications is only used to deposit DLC coatings of the type a-C:H and a-C:H:X. Typical coating thicknesses are between 1.5 and 5 μm . Hydrogenated DLC coating types deposited by PACVD cover a range of hardness between 15 and 40 GPa [61, 64, 65]. The typical deposition temperature is in the range of 200–250 °C. A bonding layer and often in addition also a support layer are deposited before the functional a-C:H or a-C:H:X coating in most of the applications. The dominating deposition method for the bonding and support layer is magnetron sputtering, but also e-beam evaporation is partially used [61].

6.5.1 Process Description

PACVD (also named plasma-enhanced, PECVD) for DLC coatings is a vacuum technology in the 0.1–1 Pa pressure range based on gas discharge, on plasma or ion source driving plasma chemical volume, and on plasma-activated surface reactions [61, 64–67]. Gas discharges with and without additional plasma activation are dominating as the PACVD process for automotive applications. The plasma can be created by glow discharges applying DC, pulsed DC, or RF between two electrodes. A gaseous precursor (e.g., CH_4 , C_2H_2 , TMS, HMDSO) or gas mixture is used for the discharge operating mostly with Ar and becomes excited and dissociated by electron impacts. The DLC coating grows at the negatively biased electrode under ion impact. A schematic view at a coating system is shown in Fig. 6.33.

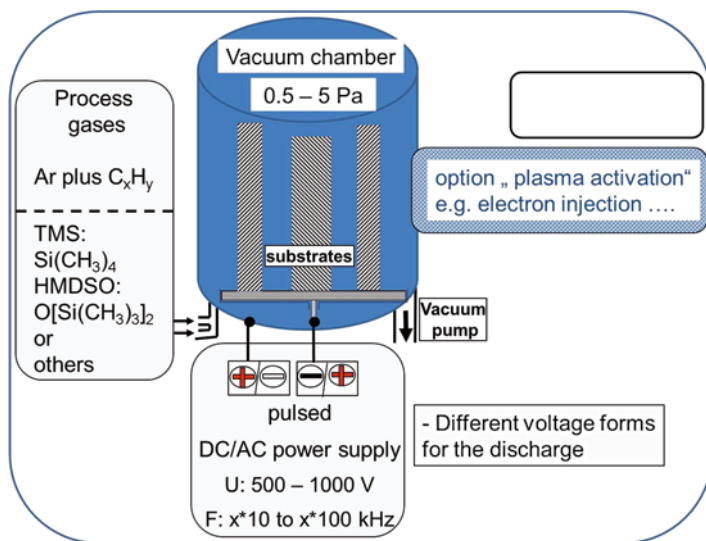


Fig. 6.33 Schematic view of a PACVD deposition system for DLC coatings

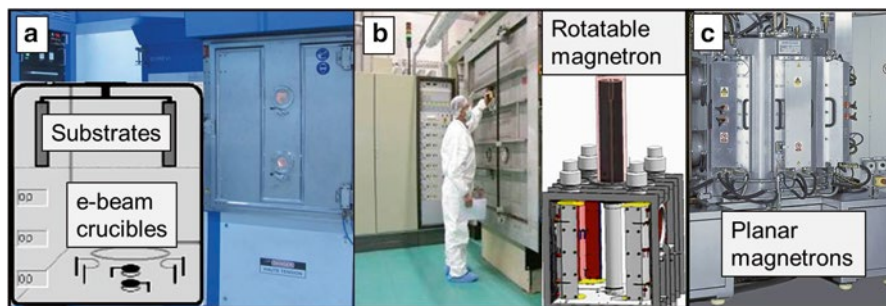


Fig. 6.34 Different coating system setups for deposition of a-C:H and a-C:H:X films by PACVD, (a) electron beam evaporation combined with PACVD, (b) central tubular sputtering source for bonding layer before PACVD, (c) sputtering equipment for both bonding layer and support layer before PACVD (courtesy of Oerlikon Metaplas)

Pulsed DC discharges with frequencies between several 10 and several 100 KHz are mostly used for industrial deposition systems [68, 69]. A short positive voltage (several 10 V) is often applied during one pulse period (asymmetric alternating field pulsing) [70]. The deposition temperature is mostly in the range of 200–250 °C. The parts are firstly ion cleaned.

PACVD systems are designed in different basic configurations depending on the type of the deposition of bonding and support layer under the functional DLC layer. Various industrial operating DLC coating systems are shown in Fig. 6.34. The first system used for racing applications was equipped with electron beam evaporators to deposit both the bonding and support layers, e.g., TiN/TiCN/TiC; see Fig. 6.34a. This commercialized coating system has the trade name CAVIDUR® and was introduced at the beginning of the 1990s by Sulzer Sorevi, France. It is still in industrial use. Sub-layer designs move to a more “complex” sequence including Si-containing layers in order to improve also the nano-roughness of the top DLC layer. Another variant is shown in Fig. 6.34b. The presented system has a central tubular sputtering cathode for depositing the bonding layer. Today, it is mostly usual to run the PACVD processes in sputtering units which are able to deposit both bonding and support layers shown in Fig. 6.34c.

6.5.2 Selected Coating Properties of a-C:H and a-C:H:Si:O DLC Coating Systems

The a-C:H and a-C:H:Si:O coatings are hard, amorphous coatings consisting of a mixture of sp²- and sp³-bonded carbon atoms with a hydrogen concentration typically between 10 and 30 at %. In general all DLC coating types show a low solid-state friction [8]. The high coating hardness, up to 35 GPa for industrial applications, provides very good abrasion and wear resistant characteristics. Figure 6.35 shows

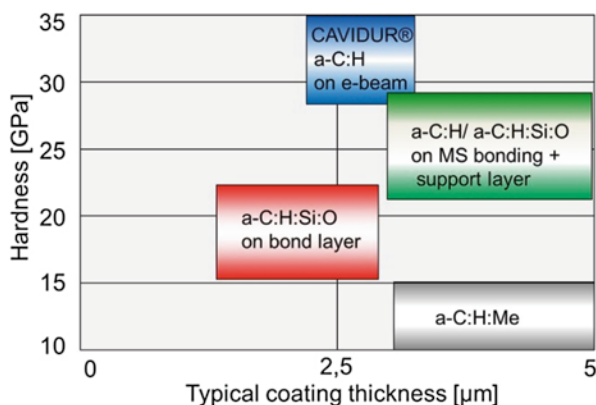


Fig. 6.35 Typical hardness ranges and coating thicknesses of the PACVD DLC coating types in comparison to sputtered a-C:H:Me; on MS, magnetron-sputtered layers; on bond layer, magnetron-sputtered bond coating; on e-beam, electron beam evaporated layers

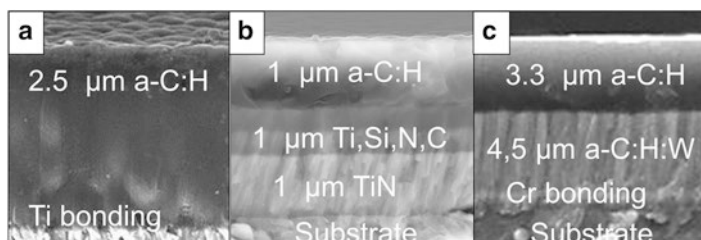


Fig. 6.36 SEM images of DLC coating architectures, (a) a-C:H-based coating on a sputtered Ti bonding layer; (b) a-C:H coating on top of a layer system deposited by e-beam; (c) a-C:H deposited on top of a layer system deposited by magnetron sputtering

typical hardness ranges and coating thicknesses, including bonding and support layers, of DLC coating types deposited in the systems shown in Fig. 6.34 in comparison to the sputtered a-C:H:Me.

Figure 6.36 shows SEM images of typical DLC coating architectures. The a-C:H- and a-C:H:Si:O-based coatings have a typical glassy-like structure nearly over the whole coating thickness as shown in Fig. 6.36a; Figure 6.36b shows the architecture of the DLC coating characterized by a functional a-C:H top layer on smooth and dense classical hard coatings deposited by e-beam evaporation. Another coating architecture is shown for coatings deposited in magnetron sputtering system in Fig. 6.36c. A sputtered support layer a-C:H:Me or CrN is deposited on a metallic bonding layer and finally an a-C:H or a-C:H:Si:O coating. That coating type is deposited with a coating thickness of up to 10 μm for piston ring applications [71].

Although a-C:H coatings may be deposited without the use of any adhesion-promoting interlayer, typically either metallic (Ti, Cr) or silicon containing a-C:H:X interlayers are used. In some cases, a more complex multilayer stack consisting of a-C:H:Si:O and a-C:H layers is deposited (named DYLYN/DLC).

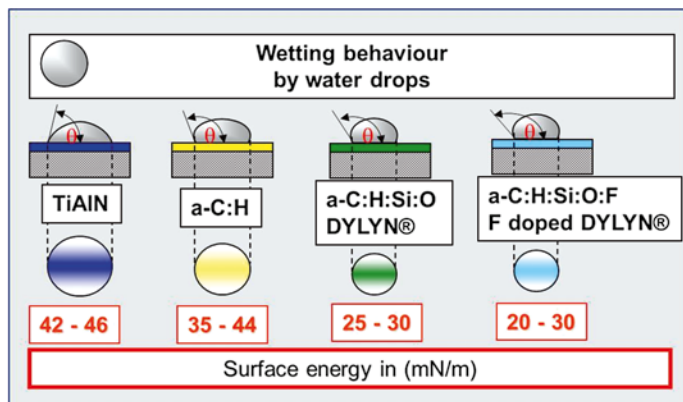


Fig. 6.37 Surface energy of different DLC coatings in comparison to a PVD TiAlN coating

Diamond-like nanocomposite, short DLN, coatings are amorphous coatings characterized by two “independent” but interpenetrating networks: an a-C:H network that exhibits typical properties of DLC coatings and an Si:O network that enhances the temperature stability, lowers film stress, and reduces the coefficient of friction [72, 73]. Within all the coatings offered by Sulzer Metaplas, this coating type exhibits the lowest value of friction, even in high humidity or wet environments. In some specific lubricated conditions, the SiO dopant strongly enhances the self-lubricating performance of the tribofilm which reduces the coefficient of friction and improves wear protection. DYLYN coatings often outperform a-C:H coatings in applications requiring both anti-stick and wear resistance. That anti-stick characteristic of coatings can be, in several cases, correlated to the low surface energy as shown in Fig. 6.37. It shall be mentioned that a fluorine-doped a-C:H:Si:O:F coating shows the lowest surface energy and unique behavior concerning spreading parameter with oil [74].

6.5.3 Selected Automotive Applications

Coatings systems with a functional a-C:H or a-C:H:X coating are dominating both in passenger cars and racing when DLC coatings are applied. The following parts are coated: parts of injection systems, high-pressure pumps, tappets, finger followers, piston pins, piston rings, pistons (racing), valves (racing), camshafts (racing), and crankshafts (racing).

Figure 6.38 shows selected applications both for racing and passenger cars.

The number of different parts coated for racing applications is still much higher than that for passenger cars. One limiting boundary condition to introduce the coating



Fig. 6.38 Selected engine applications for A.CAVIDUR, A.DYLYN, and A.CARBON coatings both for passenger and racing cars

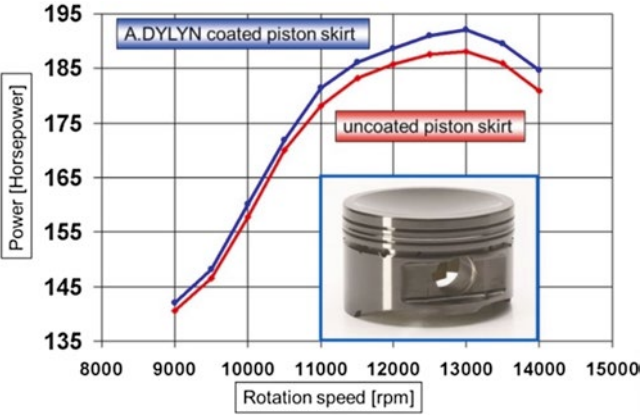


Fig. 6.39 Reduced power loss due to piston coating by A.DYLYN applied normally only for racing applications [61]

technology for passenger cars is often cost aspects. To demonstrate the high application potential based on experience in racing, a result of an engine test with uncoated and coated pistons that measures the power utilization is shown in Fig. 6.39. The coated piston significantly enables a higher power utilization. The results show that there is still a high potential to reduce friction and as a result of that also to reduce CO₂ emission by additional coating applications in passenger cars.

6.6 Combination Treatments

Combination treatments of base materials comprise at least two surface treatments of one and the same part. In the following, examples of combination treatments are described.

6.6.1 TCHT Plus PVD or PACVD

The TCHT, nitriding or nitrocarburizing, of metallic components of different materials is one of the well-established treatments (for clutch parts, springs, synchronizers, piston rings, etc.) resulting in improved performance due to an increase of the hardness, fatigue strength, and creation of residual compressive stresses. However, PVD and PACVD coatings are more wear resistant (adhesive wear, micro-abrasion, oxidation, etc.) and show often lower friction values. The combination of the TCHT and PVD or PACVD provides a product superior to both. Figure 6.40 shows the change in hardness as a function of the distance from the surface for the separate treatments and the combined treatment.

The TCHT step before the deposition of hard coatings increases significantly the load-bearing capacity of the coating-substrate system [75]. This combination treatment is an industrial standard treatment used for high-loaded piston rings as shown in Fig. 6.41. The hardness of the piston ring steel increases by a factor 3 due to nitriding. This is an excellent support for the hard coating. Not only PVD coatings but also DLC coatings are deposited on nitrided piston ring surfaces. The GN and GNC processes are realized in separate gas nitriding furnaces. The PN and PNC process can be also carried out in PVD systems before coating.

Not only nitrided piston rings are coated subsequently, also other parts, e.g., parts of the crankshaft drive system shown in Fig. 6.24 (see Sect. 6.4), are plasma nitrided before the CrN deposition.

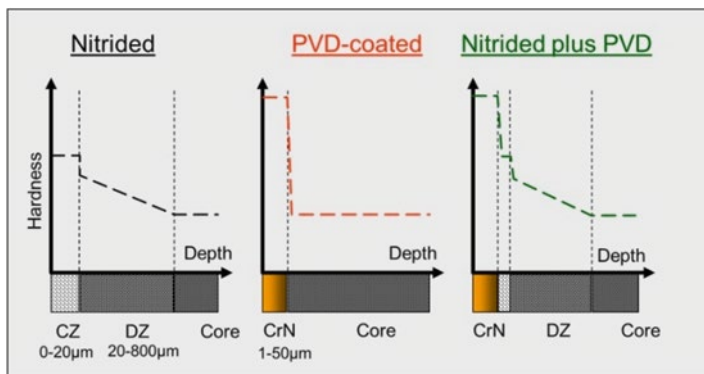


Fig. 6.40 Qualitative curves of the hardness versus distance from the steel surfaces with a nitriding treatment PN, PVD coating, and combination PN plus PVD coating; CZ compound zone, DZ diffusion zone [1]

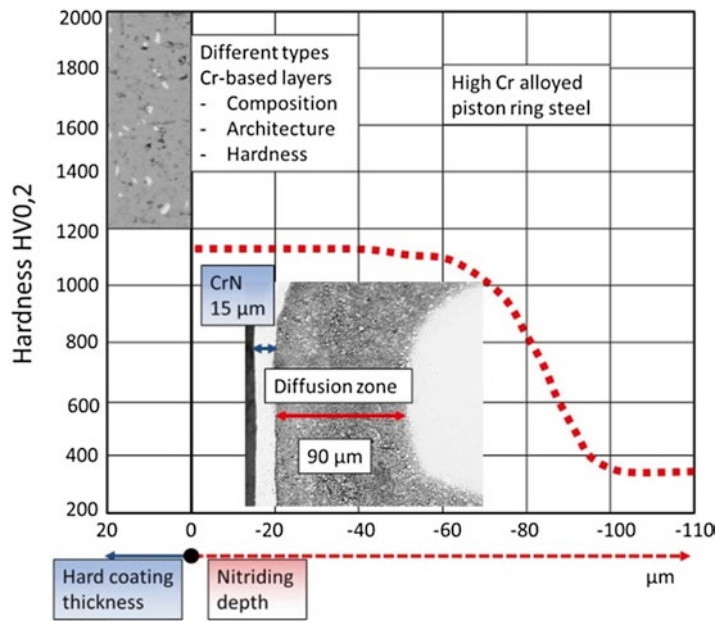


Fig. 6.41 Hardness versus distance from the surface for a high-alloyed piston ring steel plus a Cr-based PVD coating (typical hardness between 1,200 and 2,000, thickness 10–50 μm)

Fig. 6.42 Parts of multiple-cone synchronizations with a segment ring (*mid position*) having a combination treatment TCHT plus a carbon lining (courtesy of Oerlikon Friction Systems)



6.6.2 TCHT Plus Carbon

Another combination treatment is the bonding of carbon linings at plasma-nitrided steels for high-performance synchronizers shown in Fig. 6.42 [13, 76].

It has to be noticed that not only the functional properties of the synchronization are improved by that surface solution but it is also an important way to reduce the CO₂ emission by weight reduction as shown in Fig. 6.43. A weight reduction of about 40 % was achieved.

				
		Brass	Powder Metal Sint D39	Nitrated steel C35 / AISI1035 Plus Carbon EF® 8000
Potential of weight reduction				
Weight	g	78	56	47
Weight reduction	%	0% (reference)	- 17 %	- 40 %
Strength and durability improvement				
Yield strength	N/mm ²	380	420	500
Yield strength	%	0% (reference)	+10 %	+ 32 %
Elongation at break	%	13	2	12
Young's modulus	N/mm ²	105000	130000	200000

Fig. 6.43 Properties and relative weight of synchronizers based on different materials (courtesy Oerlikon Friction Systems)

6.7 Thermal Spraying

Thermal spraying (also thermal spray) techniques are a family of coating processes to deposit metallic, nonmetallic, or composite (metallic+nonmetallic) coatings with thicknesses up to several mm, thus protecting parts against wear and corrosion to create thermal barriers and to reduce friction. The coating material in powder, wire, or rod form is deposited in a molten or semi-molten condition to build up the coating. Two main energy sources are used to heat and melt the material electric arc (including plasma generation) and combustion. The coatings are built up in a lamellar structure. The family of thermal spray processes consists of plasma spraying at atmospheric pressure (APS) or in vacuum (VPS), wire arc spraying, plasma transferred wire arc (PTWA), flame spraying, detonation spraying, high-velocity oxygen fuel (HVOF) coating spraying, warm spraying, and cold gas spraying [77, 78]. In the following the focus is set on atmospheric plasma spraying for cylinder bores.

6.7.1 Process Description: APS

The basics of the APS process are shown in Fig. 6.44. The atmospheric plasma spraying (APS) process uses powders as precursor material. The energy input is based on a plasma arc discharge in an inert gas, typically argon, or an

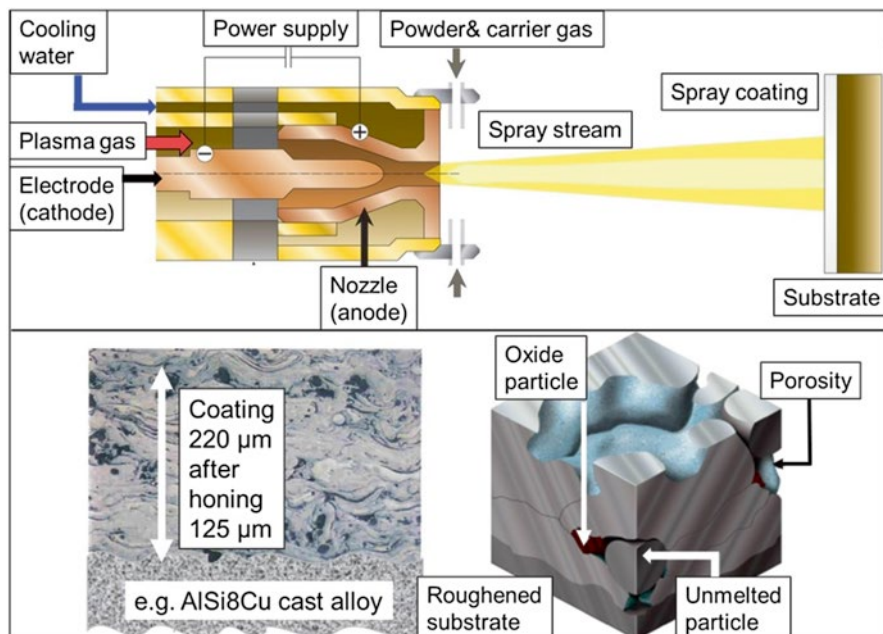


Fig. 6.44 Basics of the APS and typical coating structure (courtesy of Oerlikon Metco)

argon–hydrogen mixture, which generates plasma temperatures in the powder heating region of about 10,000 K [79]. That temperature is significantly above the melting point of ceramics; thus, also ceramic materials can be sprayed. The melted fine particles (droplets) are accelerated to high speeds up to 1,000 m/s. The particles impact at the surface, producing individual local thin layers (lamellas), often also called splats. The substrate temperature can be maintained at a low level by adjusting the spray rate (and other means). A temperature around 100 °C is industrially used for Al alloys. Figure 6.44 shows also a typical structure of an APS-sprayed iron-based metallic coating. The coatings always contain a certain percentage of open porosity and oxide particles.

This APS process is used by Sulzer Metco for SUMEBore® coatings on cylinder bores by using a rotating plasma torch (also called RotaPlasma®) [1, 10–12, 80]. Figure 6.45a shows a small torch used for passenger car engine blocks and Fig. 6.45b a larger plasma torch for locomotive liners.

6.7.2 Selected Properties

APS by rotating plasma torches allows the deposition of a wide range of coating types as shown in Table 6.3. The coatings are selected depending on the required functional properties of the cylinder bores and reduction of friction, of scuffing, of

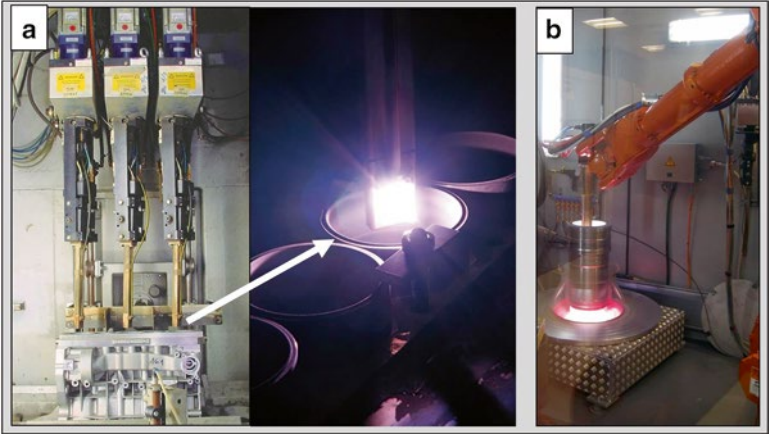


Fig. 6.45 Rotating plasma torches for cylinder bore coatings, (a) passenger cars, and (b) locomotive liners (courtesy of Oerlikon Metco)

Table 6.3 Different coating materials deposited by rotating plasma torches and main properties (courtesy Oerlikon Metco)

Matrix material	Low-alloyed carbon steel	Low-alloyed carbon steel	Low-alloyed carbon steel	Cr steel	High-Cr steel	Pure ceramics
Blended material 1		+ Solid lubricants				
Blended material 2			+ Oxide ceramics	+ Oxide ceramics	+ Oxide ceramics	
Blended material 3					+ Carbides	
Friction	+	+	+	+	+	+
Wear			+	+	++	+++
Corrosion				+	++	+++
Example of SUMEBore® powders	XPT512	F4301	F2056	F2071	F2238	F6250

wear and corrosion, and of course under cost aspects. The typical structure of sprayed different coating materials is shown in Fig. 6.46. The most dense structure is achieved for sprayed TiO_2 on a metallic bond coat.

6.7.3 Selected Applications

The most frequently used tribological solution for engine blocks in aluminum cast alloys is the insert of cast iron sleeves. That solution has several disadvantages. The pitch distance is relatively high in comparison to the bore diameter. The heat

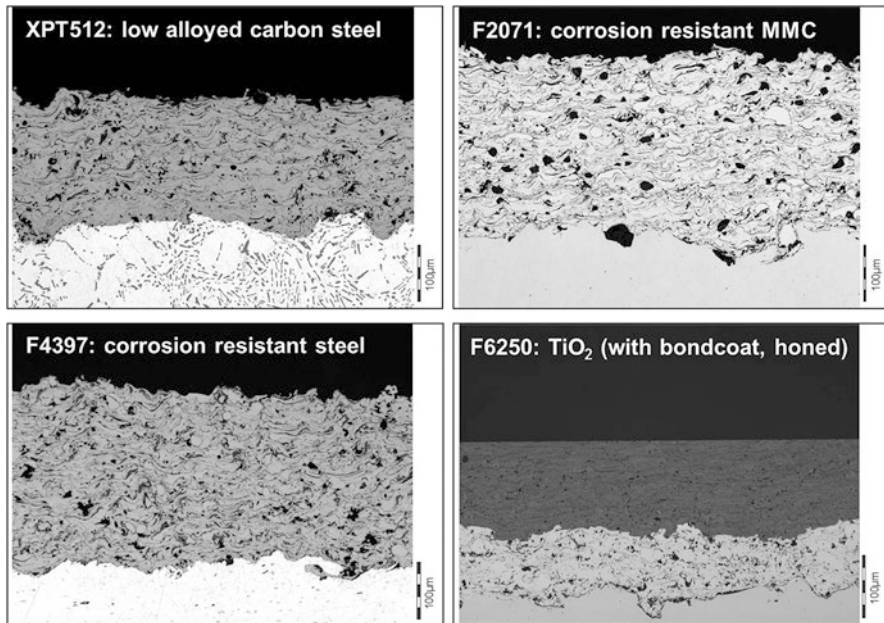


Fig. 6.46 Micrographs of different APS-sprayed coating materials MMC (metal matrix composites) (courtesy of Oerlikon Metco)

flow from the cylinder bore to the cooling system is not uniform. The distortion of the bores results in an increase of the blow-by tendency and has a negative influence on the power generated [1].

In the past decades, internal plasma spray coatings have been used more and more in the production of a variety of gasoline and diesel engines. The coating with low-carbon steel is described as an example in more detail. During the coating deposition of the low-alloyed carbon steel XPT 512, both wustite FeO and magnetite Fe_3O_4 particles are embedded in the coating. Both oxide types are working as solid lubricants. The volume content of iron oxide is controlled by the adjustment of the spray parameters, primarily plasma gas composition, time of the particle in the plasma, and plasma enthalpy.

The bore surface is mechanically activated before coating to achieve the required adhesion strength. A honing process is carried out after the deposition. The result of the honing is shown in Fig. 6.47.

The integral performance of the structure and coating material leads to three significant advantages in comparison to cast iron sleeves or monolithic material cast iron and lamellar graphite:

- High potential to significantly reduce the friction of the piston groups. A consequent fuel consumption reduction up to 3 % was measured.
- Oil consumption rate can be significantly reduced: up to 80 %.
- Wear rate is extremely low, only some nanometers per service hour.

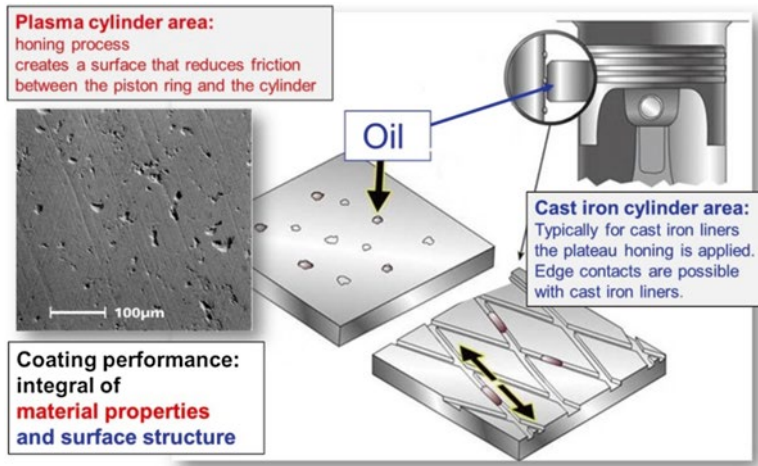


Fig. 6.47 Surface structure of a typical cast iron cylinder area and the finish honed APS-sprayed low-carbon steel coating (courtesy of Oerlikon Metco)

In addition to the above-described advanced coating solution for cylinder bores, a lot of other parts are coated by thermal spraying using different spraying methods: synchronizing rings, piston rings, turbocharger parts, oxygen sensors, shift forks, alternator covers, conrods, exhaust tubes, cylinder heads, exhaust valves, and break disks.

6.8 Summary

New developments in surface treatments, driven mainly by material aspects of the surface itself or the surface near region, provide opportunities for improving systems and their components. The new surface solutions have to be able to compete also in costs with conventional solutions. Even if there are significant functional advantages, additional aspects such as financial, reliability, compatibility with existing manufacturing methods, etc., have to be considered. Plasma-assisted surface treatments (PVD, PACVD, PN, APS) that have been developed over the last decades play a decisive role. These surface technologies are of enormous importance for automotive applications.

The following trends are visible:

The application depth of plasma-assisted surface treatments applied in the automotive industry will sharply increase in the upcoming years due to higher loads in the engine (injection systems, parts of the power train, etc.) and the general challenge to decrease the CO₂ emission.

Nitriding and nitrocarburizing as TCHT processes, both in gas and plasma, are standard solutions for various automotive parts (e.g., for clutches, piston rings). Special nitriding processes were developed, the METANIT process, as a low-temperature gas nitriding process for spring steels and plasma nitriding for sintered steels, e.g., used for synchronizers.

A standard method for surface corrosion protection, e.g., of ball pins and other parts of the power train, is the IONIT OX process.

Both classical PVD hard coatings deposited by CVAE and DLC coatings deposited by PACVD in combination with MS become more and more interesting for high-loaded parts like piston rings, timing chain parts, tappets, and parts of the crankshaft drive.

Hydrogen-containing DLC coatings deposited by the PACVD process and hydrogen-free DLC coatings deposited by CVAE evaporation used for automotive parts will increase in parallel. DLC coatings deposited by PACVD processes are dominating in injection system applications.

DLC coatings still have a high potential for lubrication reduction, friction minimizing, and load increase, e.g., for gears. Advanced DLC coatings were developed or are in development to fit specific tribological conditions.

Combination treatments are suitable for various applications like for piston rings and parts for the crankshaft drive. It is also used to create laminate materials in the form of nitrided steels plus carbon linings. This solution is an effective way to increase the shift performance and to reduce synchronizer weight.

Internal APS technology SUMEBore allows the treating of different inside diameters (bores) in the engine to reduce bore wear and friction and to minimize the weight and lubricant losses.

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Chapter 7

Hard Coatings and Coating Processes for the Automotive Industry

André Hieke, Val Lieberman, and G.J. van der Kolk

Abstract Thin film coatings have over the years found a way into a variety of applications in the automotive industry. First applications of carbon-based coatings (DLC) were introduced for fuel delivery systems in the mid-1990s, followed by engine components a few years later. DLC coatings for fuel injection components and engine components such as valve tappets, cam followers, and piston pins represent the bulk of the mainstream applications and have become a de facto standard for many automotive manufacturers. The next generation of coatings for the automotive industry will be designed to interact with additives in fuels and engine oils. Of particular interest are tribo-chemically active coatings, which promote the formation of beneficial tribological films. Besides carbon-based coatings, the chapter reviews coating applications in turbochargers. The turbochargers are very efficient devices to boost power output of combustion engines, thus enabling engine downsizing and respective gain in fuel consumption. Due to the unique operating conditions, turbochargers are exposed to various mechanical challenges at normal and elevated temperatures. Potential applications of hard coatings for wear protection in turbochargers are reviewed. Finally, an application of hard coatings for manufacturing technology of catalytic converters and diesel particulate filters is discussed.

Keywords Hard coatings • PVD • CVD • HIPIMS • Wear protection • DLC • Automotive • Engine components • Fuel injection • Tribo-chemical active coatings • Turbochargers • High temperature

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7.1 Introduction

Driven by ever-increasing legislative pressure to reduce exhaust emissions, as well as by rising energy prices, automotive manufacturers are forced to downsize and improve the efficiency of engines and drivetrains without compromising the performance levels and the lifetime of their vehicles.

The consequential increase of the specific loads on components and the need to lowering the friction losses in the mechanical assemblies initiated the search for ways of reducing friction and wear many years ago. The solution was found by using thin film coatings like DLC (diamond-like carbon) on a wide range of engine, drivetrain, and fuel injection components. Ionbond has developed and industrialized these coatings since the early 1990s with its Tribobond™ branded line of low-friction and wear-reducing coatings.

For tribologically high-loaded systems, the application of coatings with low-friction properties, such as Ionbond's Tribobond™ 40 DLC series, offers a wide range of technical solutions. When moving parts require low-friction losses and high wear resistance as it is the case in the valve train and on piston pins and piston rings, then low-friction DLC coatings are the best performing coating types. The coatings support heavily loaded contact surfaces and increase the load-carrying capacity. Typical coating thicknesses of 1–4 µm are common for a majority of serial automotive applications, and the option of low-temperature processing (<200 °C) allows tempered low-alloy steels to be coated without loss of hardness.

7.2 Coatings for Fuel Injection Systems

The tribological behavior of three coatings was investigated in two commercially available fuels (diesel/E5 gasoline). Tribological data and cross sections of the selected DLC coating types are in the Table 7.1 and SEM pictures below (Fig. 7.1). The a-C:H top layer of Tribobond™ 41 and the a-C:H layer of Tribobond™ 41 ML in the multilayer structure were deposited by PACVD. For Tribobond™ 47, a PVD process was used to apply the hydrogen-reduced a-C:H top layer (Fig. 7.2).

Table 7.1 Overview of selected coating types

IHI Ionbond brand name	Shortcut	DLC—coating type	Hydrogen content (at %)	Microhardness (HV 0.05)	Coating thickness (µm)	Max. service T (°C)
Tribobond™ 41 (reference)	DLC 1	Cr+a-C:H:W +a-C:H	18	2.521	3.0	250
Tribobond™ 47	DLC 2	Cr+CrC+a-C:H	9	3.242	2.5	250
Tribobond™ 41 ML (multilayer)	DLC 3	Cr+a-C:H:W (+ a-C:H+a-C: H:W) _x	a-C:H:W: 12 a-C:H: 18	2.267	3.5	350

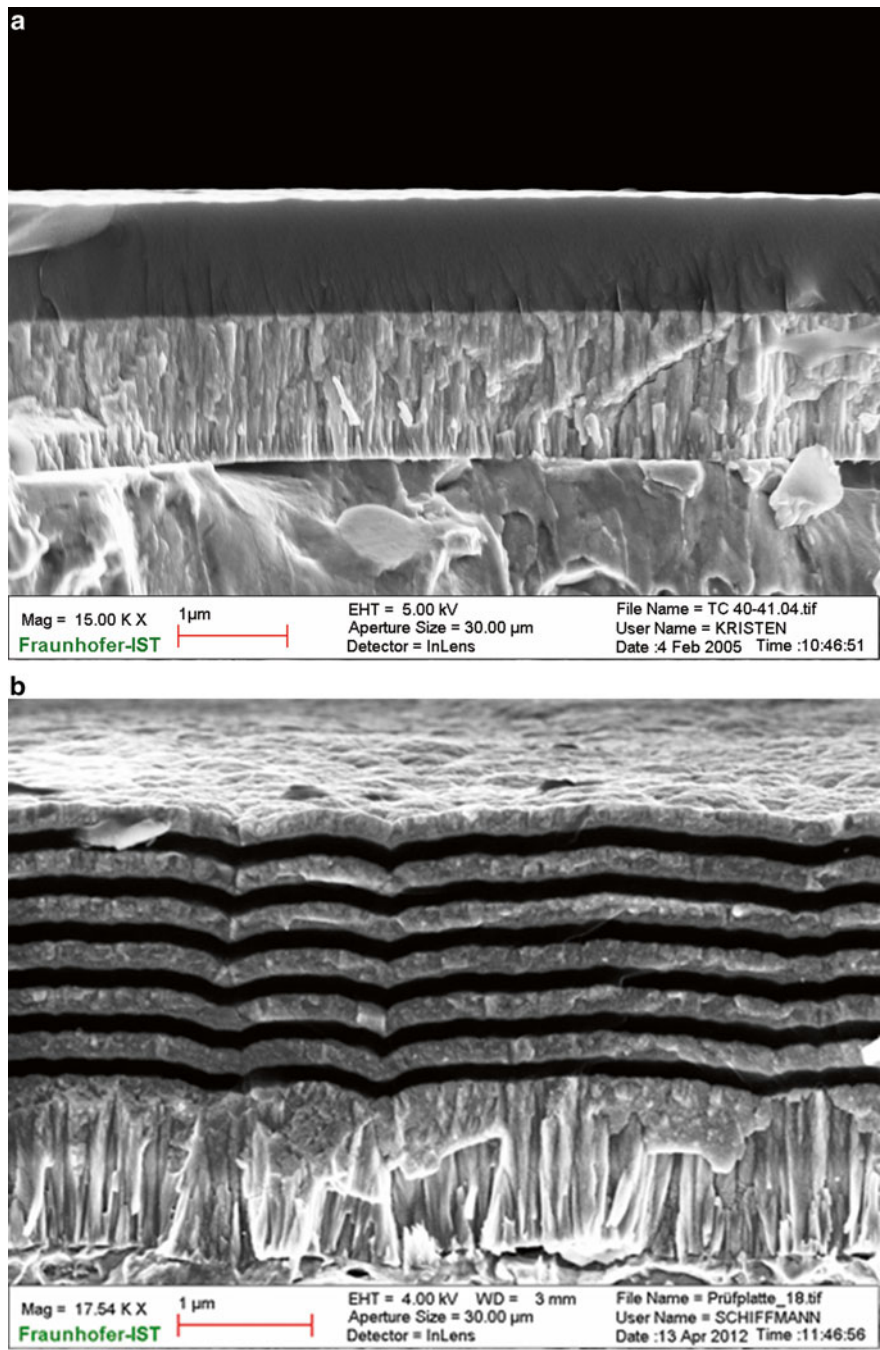


Fig. 7.1 Cross sections of the selected DLC types. (a) Tribobond™ 41, (b) Tribobond™ 41 ML, (c) Tribobond™ 47 (Source: IHI Ionbond)

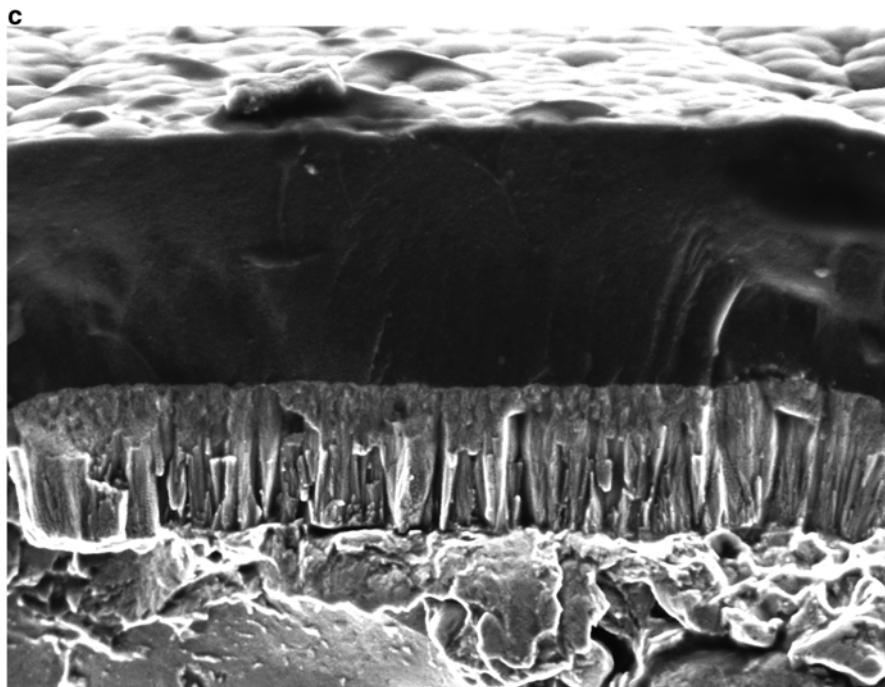


Fig. 7.1 (continued)

Fig. 7.2 Oscillating ball-on-disk tester (Source: Photo IHI Ionbond)



The tribological testing was performed in an oscillating ball-on-disk tester. A bearing steel ball with a radius of 5 mm was loaded with 10N against the coated flat. Fuel was applied during testing using a syringe pump with a flow rate adjusted to match the evaporation rate so that the contact would always be immersed in fuel. Each combination of coating and fuel was tested in a 100,000-stroke test, where the friction was continuously recorded and the wear was quantified and studied in the

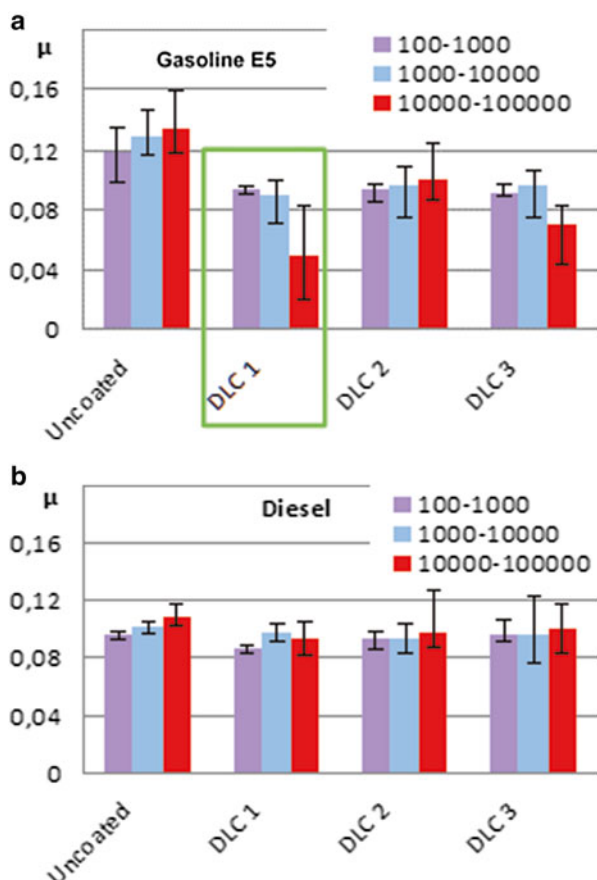


Fig. 7.3 Measurement results of the coefficient of friction (COF) in E5 gasoline (a) and diesel fuel (b)

microscope after the test. Further, two shorter 10,000-stroke tests were performed for each combination to verify the friction behavior and to give an indication of the initial wear.

7.2.1 Wear and Friction Results

All DLC coating types 1–3 gave an initial coefficient of friction of 0.09 lubricated by E5 gasoline and diesel fuel, which then dropped to 0.04–0.07 for DLC 1 and DLC 3. For DLC 2, the friction showed a slowly increasing trend. There is no difference in the behavior of the COF for all coating types in diesel fuel (Fig. 7.3).

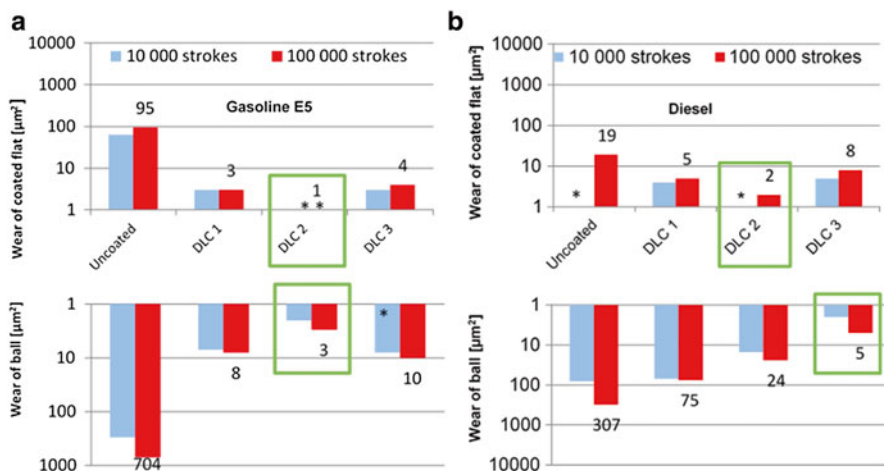


Fig. 7.4 Wear measurement results of the coated disk and uncoated ball in E5 gasoline (a) and diesel fuel (b)

All DLC coating types 1–3 showed very limited wear after 10,000 strokes in both fuels. The best performing coating in case of wear resistance in E5 gasoline fuel was Tribobond™ 47 (DLC 2) after 100,000 strokes. There was no wear measured on the coated disk and also a very low wear rate on the uncoated ball which means DLC 2 gave an excellent counterpart protection. Tribobond™ 47 had also the lowest wear rate in diesel fuel, but Tribobond™ 41 ML (DLC 3) showed the best performance to protect the uncoated ball (Fig. 7.4).

Further analysis in the tribological contact of Tribobond™ 41 ML and the ball were done by FTIR. It shows that DLC 3 is able to interact with sulfur in the diesel fuel. The tungsten content in a-C:H:W layer and sulfur is locally forming WS₂ (see Fig. 7.5) as an additional low-friction dry lubricant in the tribological system [1].

All investigated DLC coating types (DLC 1–3) did perform well under fuel-lubricated conditions.

Tribobond™ 41 (DLC 1) shows the lowest coefficient of friction in E5 gasoline fuel. The best performing coating type lubricated by E5 gasoline and diesel fuel in case of wear resistance is Tribobond™ 47 (DLC 2). This behavior is linked to the high coating hardness (>3.000 HV), low hydrogen content, and high cross-linked coating structure.

Outstanding results were also measured for Tribobond™ 41 ML (DLC 3). This tribo-chemically active coating type is able to interact with additives like sulfur in diesel fuel. Due to the multilayer structure of thin a-C:H and a-C:H:W layers, the tungsten content in the DLC 3 coating is able to form in the tribological contact WS₂ as an additional solid lubricant. Tribobond™ 41 ML caused significantly less wear of the uncoated counterpart. This result indicates the huge potential in developing

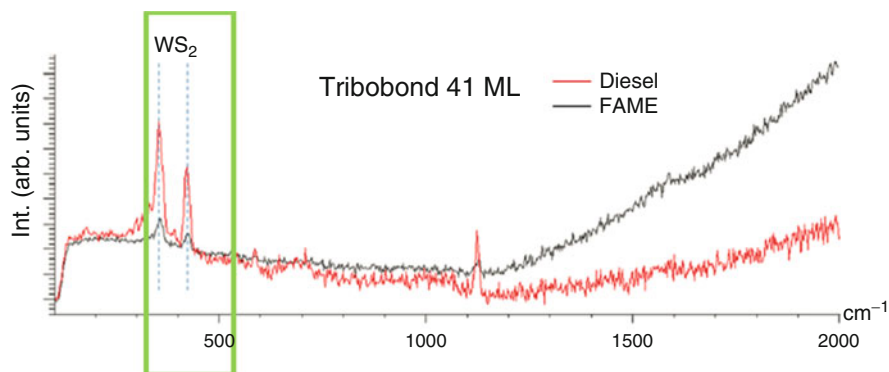


Fig. 7.5 FTIR measurement results in the tribological contact of the uncoated ball and the Tribobond™ 41 ML coated disk lubricated by diesel fuel (*red line*)

DLC coatings with chemistries that promote formation of beneficial tribological films and demote the formation of detrimental films, under the specific prevailing condition.

7.3 Coatings in Turbochargers

The ever-increasing pressure to improve the fuel efficiency of internal combustion engines mandates substantial effort in development of novel ways and optimization of the conventional ones to reduce the volume and improve the quality of the exhaust gases. Among a variety of ways to improve the efficiency of internal combustion engines, the use of turbochargers is clearly one of the most popular paths. Turbochargers allow to substantially increase volumetric efficiency of the engines, which results in the increased power output.

Volumetric efficiency can be affected in a variety of ways, for example, by using two pairs of valves and a DOHC engine layout. However, further improvements in naturally aspirated engines require individual and expensive engine tuning, which is not practical for mass-produced engines. Turbocharging is a much simpler and economical alternative to achieve radical improvements in engine efficiency, both volumetric and thermal. Starting from the 2014 season, engines in Formula 1 circuit use turbochargers as a part of their sophisticated energy recovery system—after 25 years of utilizing naturally aspirated engines. The last 10 years also saw a paradigm shift in the very reason to use turbochargers: instead of generating more power from a given engine, they used a smaller turbocharged engine to achieve the same power [2]. It is reported that turbocharged engines can increase the fuel economy by as much as 30 % in comparison to an equally powerful naturally aspirated engine [3].

A turbocharger is virtually a radial flow compressor, which is powered by a turbine driven by the exhaust gases of the engine. The history of turbocharging goes back to the 1905 patent of a Swiss engineer Alfred Buechi on the exhaust gas-driven compressor. An alternative to turbocharging, supercharging, was a mainstream technique to boost the intake of air pressure for the first half of the twentieth century. This was largely related to limited availability of high-temperature materials suitable for manufacture of turbine wheels. Advances in materials science, driven by jet engine development, made available a range of nickel- and cobalt-based superalloys, capable to retain sufficient mechanical strength at temperatures of over 1,000 °C and therefore to be suitable for turbine side operating conditions.

By any standard, operation of a turbocharger occurs in a very challenging, not to say hostile, environment. Besides being corrosive and oxidizing, exhaust gases can easily achieve a temperature of 1,000 °C or even higher. Rotational speed of the turbochargers may approach 150,000 RPM, which brings about massive centrifugal forces and, consequently, tensile loads in rotating components. Vibration effects and cyclical bending accompany the operation of the turbocharger, leading to various wear phenomena. The midsection, or central hub, of a turbocharger is subject to a variety of mechanical challenges: combating bilateral transient thrust loads, providing a seal between compressor and turbine sections, and supporting the shaft in the whole range of operating RPMs. Modern turbochargers are equipped with an internal wastegate, which is essentially a proportional valve, allowing a portion of the hot exhaust gases to bypass the turbine. An obvious challenge for this valve is extreme operating temperature. As an alternative to the wastegate, variable geometry turbochargers (VGTs) are also gaining popularity due to their ability to adjust the geometry of turbine chamber depending on the engine speed and therefore to decrease the lag and lower the boost threshold.

Generally speaking, the areas of a turbocharger that can benefit from thin film coatings can be grouped in three categories, arbitrarily separated by the operating temperature range: low temperature (<200 °C), medium temperature (200–700 °C), and high temperature (>700 °C). Naturally, besides operating temperature, coating selection is dictated by the functionality, which is required or the problems that the coating is intended to solve (Fig. 7.6).

7.3.1 Turbochargers: High-Temperature Applications

Among the most problematic areas of the turbochargers is a wastegate assembly. It is operating in direct contact with exhaust gases and therefore running temperatures can reach up to 1,000 °C. A usual design of the assembly consists of a bushing, which houses the shaft with an integrated valve flap (Fig. 7.6). The shaft makes oscillatory movements inside the bushing to open and close the valve with an amplitude of a few millimeters. The frequency of the movements is usually limited to 150 Hz, with the bulk of the movement occurring at lower frequency.

Fig. 7.6 View of the turbine section of a generic turbocharger. Wastegate and turbine impeller are shown (Source: Fotolia LLC, www.fotolia.com)



The operating temperature of the assembly lies in the range of 700–900 °C. Obviously, no conventional lubrication is possible in this case. Common materials that are used in this assembly are either superalloys (Inconels) on both parts or nickel-based alloy on the valve shaft and stainless steel on the bushing, as its temperature is somewhat lower. A problem occurring in the assembly is wear, which in the worst case can lead to jamming of the valve. Considering the friction conditions, it is plausible to assume that the wear mechanics in this case is high-temperature fretting. Since both materials easily form tenacious oxides, one can expect that they would provide adequate protection against fretting. However, if surface roughness and operating conditions lead to spallation of native oxides, they will act as an abrasive, causing more spallation and respectively more wear. One of the possible coating solutions in this case is to apply coatings, which could form oxides that are better adhered to the substrate and thicker and harder than the native oxides of the used materials. Deposition of a well-adhered and hard oxide film of sufficient thickness could be seen as an ultimate solution.

PVD technology offers a wide variety of possibilities in terms of coating composition. However, PVD deposition of oxide films of substantial thickness (5 $\mu\text{m}+$) on steel substrates remains a challenging task. The challenge is related to processing difficulties (quick conversion of the target surface into nonconductive oxide, anode loss, and loss of conductivity by the substrates) as well as challenges to provide reliable adhesion between ceramic and metal materials. Usual approach to resolution of these problems is deposition of a conductive nitride or carbonitride film of Ti, Al, Cr, Si, or their combination by more or less regular PVD process and letting this film convert into oxide(s) once it is exposed to high temperatures in the application. Modern coatings for cutting tools, in particular for hard or lubricant-lean machining, are designed to operate in this fashion. IHI Ionbond has selected this route for development of suitable coatings and is currently carrying out a development program, where a variety of PVD coatings produced by this method are being tested in wastegate assemblies.

One can speculate that coating of both the bushing and the valve shaft will produce an ultimate benefit, at least from the technical perspective. The challenge here

is that ID coating of the bushing with a fairly high aspect ratio is required, thus making application of the PVD process difficult or impossible. In this case, a thermal CVD process is a viable alternative. IHI Ionbond has more than 40 years of experience with CVD processing, being a market leader in application of this technology. CVD technique can easily produce uniform deposits on the ID of wastegate bushings. Application of CVD coatings in this case is also attractive from the point of view of the substrate materials, which will be virtually unaffected by high processing temperature. There are two possibilities to produce a coating in this case: a standard overlay type coating or diffusion coating. An overlay coating is deposited as a chemical compound (i.e., TiN) with only limited interdiffusion between the coating and substrate, similar to PVD films. Conversely, diffusion coatings are formed when inward diffusion of the deposited element is accompanied by outward diffusion of one or more constituents of the substrate. Diffusion coatings can also produce new phases, when the concentration of the elements reaches appropriate ranges for their formation. A classic example of a diffusion CVD process is the aluminizing of superalloys, when nickel aluminides are formed due to concurrent diffusion of aluminum and nickel (this coating is widely applied onto components of hot section of jet engines).

Selection of CVD coating for a wastegate bushing should consider application requirements, i.e., the coating has to provide sufficient hardness at high temperature, oxidation resistance, and ability to protect against high-temperature fretting. Range of available CVD coatings in this case is determined by the number of available precursors. Since halide precursors are generally used in thermal CVD, virtually any halide-forming metal can be deposited. An option of production overlay or diffusion-type coatings depends on the substrate material, desired coating composition, and state-of-the-art level on the deposition technology. While CVD-produced oxide coatings would be an obvious choice for the bushing application, they generally do adhere poorly to steel substrates, especially those with low carbon content. A dedicated development effort is being carried out in Ionbond with a purpose of producing well-adhered oxide films on a variety of corrosion and heat-resistant steels.

Another interesting application of coatings in the turbine side of turbochargers is anti-coking coating to prevent a buildup of solid by-products of combustion on the turbine. While it is of a lesser issue for pure automotive turbochargers, the problem is very real for turbochargers of marine, locomotive, and ship diesels, where heavy fuels prone to coking are used.

7.3.2 Turbochargers: Mid-temperature Applications

Potential coating applications in the mid-temperature range are commonly concentrated in the turbine side of the turbocharger, albeit without direct exposure to exhaust gases. Among those are mechanical systems for driving the wastegate or variable geometry mechanics. While the operating temperature of these components is moderate, it is still high enough to prevent use of conventional lubricants

Fig. 7.7 View of the central hub and compressor wheel and shaft of a generic turbocharger (Source: Fotolia LLC, www.fotolia.com)



and cause some oxidation. In addition, mechanical joints can be subjected to abrasive wear due to presence of dust and sand in the environment. Correctly selected PVD coatings will generally provide a reliable solution for the majority of these applications. The coating assignment depends on the exact configuration of the mechanical link, operating temperature, and materials. Conventional coatings like TiN and CrN very often are sufficient to provide adequate performance for these components. In extreme cases of temperature and wear, more advanced coating materials, e.g., TiAlN, would be preferred.

7.3.3 Low-Temperature Applications

Compressor side and center hub mechanical components are subjected to mostly wear-inducing factors, without an impact of high-temperature oxidation. A typical problem associated with the compressor side is corrosion of the impeller, usually made out of lightweight materials, like aluminum alloys (Fig. 7.7).

Depending on the geography and climate, quality of ambient air varies—cars operating in the vicinity of an ocean in subtropical climate will obviously ingest fairly corrosive air. Presence of dust and sand will further accentuate corrosion attack on the impeller. Application of PVD coatings, such as CrN, for corrosion/erosion protection of impellers is clearly possible; however, limited degree of corrosion protection by the conventional PVD films should be taken into account. Advanced PVD processing for deposition of specially formulated multilayer films, which may include HIPIMS technology or superlattice coatings, may offer a better solution in this case. Another consideration for PVD processing is an intricate geometry of airfoils of the impeller, which creates a problem with the coating uniformity and quality in the “shaded” areas. These problems can be alleviated by customized rotation setups and placement of coating sources. A final challenge, very common for automotive applications, is whether a cost of coating is sustainable for the manufacturer.

The center hub of the turbocharger houses the bearing and sealing system for the rotating assembly (turbine and compressor impellers and shaft). The sealing system is designed to maintain the pressure difference between the hub pressure (equal to crankcase) and compressor and turbine sections, which are at a higher pressure. A usual design element of this system is the seal ring, located at both sides of the bearing housing. Seal rings are generally shaped like piston pins and placed in the shaft grooves on the compressor and turbine sides of the turbocharger. Outer surface of seal rings snugly fits the housing, thus preventing rotation of the rings. End faces of seal rings perform the sealing function and are in contact with the groove of the shaft. While the contact is well lubricated under normal conditions, wear may present a problem, in particular if the oil becomes contaminated or solid buildup is formed due to excessive temperature in the oil supply channels. PVD coatings present a very reliable solution for these problems. Coating selection should consider protection against abrasive wear, but low-friction films can be beneficial for this application as well. Since the seal rings are often made out of steels, which are tempered at below 200 °C, low-temperature PVD coatings are generally used. CrN coatings with various Cr/N ratios are suitable candidates for this application, as well as amorphous carbon films.

7.4 Coating for Automotive Manufacturing: Ceramic Extrusion Dies

Besides direct applications onto automotive components, thin film coatings find numerous applications in automotive manufacturing technologies. Most of those are used to produce a functional film on the surface of tools—to extend their life, improve the quality of finished components, enable high-speed manufacturing technologies (e.g., in cutting), and also enable manufacturing when new materials are used (e.g., composites). Selection of coating materials for automotive manufacturing is determined by the required functionality, which determines not only the coating composition, but the deposition method as well, PVD, CVD, or PACVD. Well-known examples of coating applications are various cutting and forming tools. Extrusion tools are among usual candidates for application of the coatings.

There are two commonplace strategies for reduction of automotive pollution: to produce less off-gases and to reduce the amount of polluting gases exhausted in the atmosphere, in particular NO_x and CO. In case of diesel engines, besides gaseous by-products of combustion, substantial volumes of particulate of various chemistries are generated as well. Therefore, exhaust treatment technologies have a huge impact on the overall environmental footprint of internal combustion-driven vehicles.

A modern way of treating exhaust gases almost invariably involves forcing exhaust gases through catalytic converters and/or diesel particulate filters (DPF). In both cases, a ceramic honeycomb is used as a pathway for the gases, providing the reactive surface for the chemical reaction to occur. In addition to this, in case of DPF, the gases are forced through the honeycomb wall, thus filtering off solid particulate.

Ceramic honeycomb is a central element in this system and its performance impacts not only the quality of the exhaust gases but also the engine efficiency.

Ceramic honeycombs for exhaust treatment systems are usually produced out of either silicon carbide (SiC) or cordierite, with the former intended for production of DPFs and the latter for catalytic converters. The honeycombs are produced either as monoliths (catalytic converters) or out of segments that are cemented together (DPF). Since DPF requires high temperature for regeneration process, segmented design in combination with low coefficient of thermal expansion of SiC provides geometrical stability of the filter at the regeneration temperature.

Ceramic honeycombs are produced using ceramic extrusion process, when the ceramic material is mixed to form a paste-like clay, which is pushed through a die, having the necessary geometry to form the honeycomb structure of the finished product. The honeycomb die is a very complex and expensive tool, having exceptionally intricate geometry. Usually, these dies are made out of tool steels, but sometimes cemented carbide is also used to assure better wear resistance. For reference, wall thickness of the honeycombs is in a range of a few hundred microns with a cell density of up to 400 cells per square inch [4].

Ceramic clay used for the production of honeycombs is very abrasive and tend to wear the inner passages of the extrusion die, therefore increasing the wall thickness in the finished product. Wall thickness is crucial for the functionality of the honeycomb. Increased wall thickness leads to increased pressure drop, which negatively impacts engine performance [5]. Manufacturers of ceramic honeycombs implement multiple controls to assure that wall thickness remains within predetermined tolerances. An ability of the die to maintain dimensional stability is a key factor in maintaining stable quality of the extruded product.

In a sense, the extrusion die is an ideal application for a wear-resistant coating: abrasive wear resistance is proportional to coating hardness, so one can expect a substantial increase in lifetime of the coated tool. The problem with this particular tool is that the coating is needed inside a slit with an aspect ratio of over 30. Attempts to use PVD coatings, deposited on both entry and exit sides of the die, while producing some improvements, were not successful in providing measurable benefit due to their inability to penetrate deep inside the die cavities. A CVD method allows for substantially better flexibility in promoting coatings in narrow passages, in particular when the process is run in the regime, when the deposition process is controlled by gas diffusion.

CVD coatings can also provide outstanding thickness uniformity, which is important for the die operation. The die has varying geometry of the extrusion channels; therefore, certain areas of the channels wear faster. Unfortunately, the area with the fastest wear is located in the middle of the channel, i.e., in the area, where the coating may be the thinnest. Being aware of these and other issues, Ionbond engineers have developed a specialized technology of deposition of CVD coatings onto the ceramic extrusion dies (Figs. 7.8 and 7.9). The technology employs a specific CVD process, which can be run at a relatively low deposition temperature. This allows more flexibility in maintaining core hardness of the die if it is made out of steel, even though the hardness of the die after the coating plays

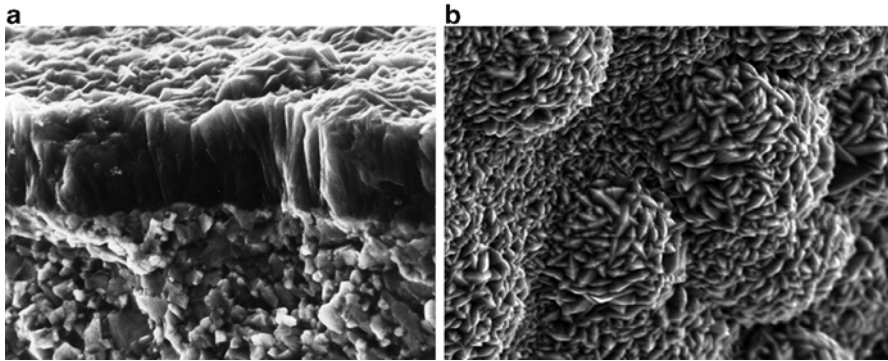
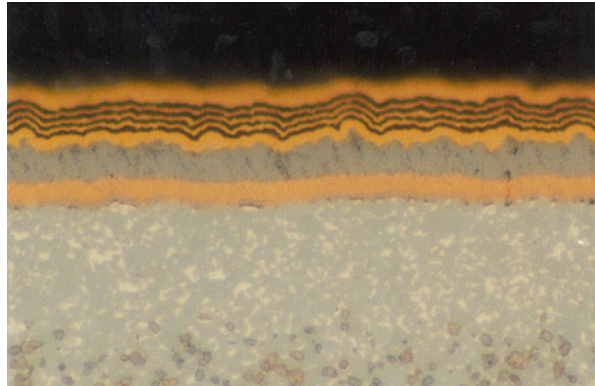


Fig. 7.8 Typical SEM images of CVD coating for extrusion dies. (a) Fracture view, (b) morphology (Source: Ionbond AG)

Fig. 7.9 Cross section of a multilayer CVD coating (Source: Ionbond AG)



lesser importance, since the coating provides wear protection. The coating process was optimized to produce the highest deposition rate, while maintaining high hardness of the film. It is carried out in the Ionbond Bernex CVD coater (Fig. 7.10). Special attention was paid to the configuration of the deposition zone, so that to provide the highest possible thickness uniformity in the die's channels. The developed method allows deposition of coatings of up to 60–70 μm thick.

One of the specifics of this coating application is that high cost of the die mandates well controlled recoating process. This involves diligent monitoring of the coating wear during operation of the die at the customer site. The die must be taken out of production before the coating is worn through; otherwise, fast wear of the underlying material will make the die unusable. Once the die is returned for recoating, it can be directly recoated to restore the desired coating thickness. Another option, which was also developed in Ionbond, is a complete removal of



Fig. 7.10 CVD Coating Reactor BPXpro 530L-T (Source: Ionbond AG)

the initial coating, followed by deposition of a new layer. This option allows for virtually unlimited recycling of the dies, making it very attractive and cost-effective measure for the manufacturers. Ionbond continues developments of the new processes for coating of ceramic extrusion dies.

7.5 Summary

The automotive industry of the twenty-first century faces a challenging task of minimizing the environmental impact of new vehicles. This happens on the backdrop of stiff competition in the industry and increasing demand for comfort, safety, and esthetics from the consumers. Thin film coatings, produced by PVD, CVD, and PACVD technologies, find more and more applications in various systems of the vehicles due to their unique properties and environmentally friendly production methods. In modern manufacturing, the coatings are applied as enabling solutions (e.g., components of fuel injection systems), cost savings (piston pin), fuel efficiency and reliability solutions (cam followers), and esthetical elements (internal and external trim). Legislation related to reduction and eventual ban of electroplating forces manufacturers to search for alternatives and PVD coatings in many cases can successfully replace galvanic processes with equal or better performance. The coatings are also widely used in the automotive manufacturing processes, providing extension

of life for cutting and forming tools. This has a particularly pronounced effect in case of tools used for machining and forming of high-end materials, like composites and high-strength steels. It is authors' belief that thin film coatings will continue being a sound solution for a variety of applications in the automotive industry. A combination of wider acceptance, legislative pressure, and ability to provide unique solutions should fuel further penetration of the coatings in the automotive industry.

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Chapter 8

Machining and Characterization of Functional Surfaces of Thermal-Coated Cylinder Bores

Gerhard Flores, Andreas Wiens, and Manuel Waiblinger

Abstract Machining of thermal-sprayed layers is a new challenge for machining cylinder bores with different honing variants. New strategies for machine and tool layouts as well as in particular the availability of appropriate diamond stones considering the material-specific properties of the cutting process are essential. Based on the coating material characteristics which are relevant for machining, a new honing process is presented.

Following the material properties of thermal-sprayed layers, the machining task, the process layout and the obtained quality values are described. Also the different variants of machining strategies are indicated, which are applicable for the different thermal-sprayed layers. The paper describes the machining results regarding the functional properties.

Keywords Thermal coating • Wire coating method • Powder coating method • Roughening method • Bond strength • Rough honing • Position honing • Material stock removal • Process chain • Layer thickness • Diamond honing shoes • Finish honing • Topographic features

8.1 Introduction

The machining and characterization of thermal coatings with different spray technologies based on a rough surface as sprayed has the target to obtain a functional surface topography of a quasi-monolithic cylinder block. The different layer qualities offer favourable conditions for further friction and wear reduction in modern combustion engines. The machining task is described regarding relevant material properties of thermal coatings. Different honing processes are presented which

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lead to cylinder bore surface topographies with low friction. The paper concludes with the discussion of the machining results, the reference to experience in serial production and an outlook at further process developments.

8.2 Material Properties of Thermal-Sprayed Layers

The following indicated material properties are selected concerning their importance for the mechanical machining. Layer parameters like porosity, ductility or residual stress condition are less relevant for machining.

The thermal-sprayed layers used for cylinder bores of combustion engines are realized by wire or powder coating methods. As wire coating method, the LDS (wire arc spraying) and the PTWA method (Plasma Transferred Wire Arc) are applied. Also used in serial production is the APS powder coating method (atmospheric plasma spraying). The layer structure is differently scaled depending on the coating method and on the used parameters. In any case, the layer consists in single spray particles (droplets) which hit the substratum surface in liquid or pasty condition and which are piled up as a layer with lamellar structure. Generally the substratum is the pretreated aluminium surface of the cylinder bore. This surface shows a microtopography with as many as possible undercuts, so that in case of suitable roughening profile depths, there is a strong and tight bond between the sprayed layer and the substratum by microform fit, shrinking strains and adhesion. This is possible, e.g. by corundum blasting, high pressure water jetting or different variants of mechanical roughening of aluminium substrate. There is also the possibility to use a NiAl adhesive layer between a cast iron substratum and the layer. These processes are approved in serial production and assure sufficient bond strength [1].

Due to their high kinetic energy, the spray particles are placed flat deformed on the surface evenly. Depending on the specific coating method, the lamellar layer structure of approx. 0.200–0.600 mm coating thickness (radial) grows up successive by hitting the spray particles on the substrate surface. For the mechanical machining of thermal-sprayed layers, not only the adhesive quality with regard to the substratum is of great importance but also the strongest possible cohesive strength of the particular sprayed particle. This material structure is the result of local melting or mechanical micro-clamping.

Figure 8.1 shows the example of a thermal-sprayed layer structure. The layer has pores (1), grey oxide lamella near the profile edges of the roughening structure (2) and shrinking splits between the sprayed particles piled up on each other (3) which are caused by the residual stress during the cooling process. The roughening profile with the dovetailed undercuts is also visible (4).

The oxides of a layer have great influence on the tool lifetimes as the oxides cause an abrasive wear effect on the honing stone surface. In addition to the layer structure with oxides and pores, also the surface profile as sprayed with a roughness between approx. 20 and 200 $\mu\text{m } R_z$ has a disadvantageous impact on the tool lifetime for mechanical machining of the layer.

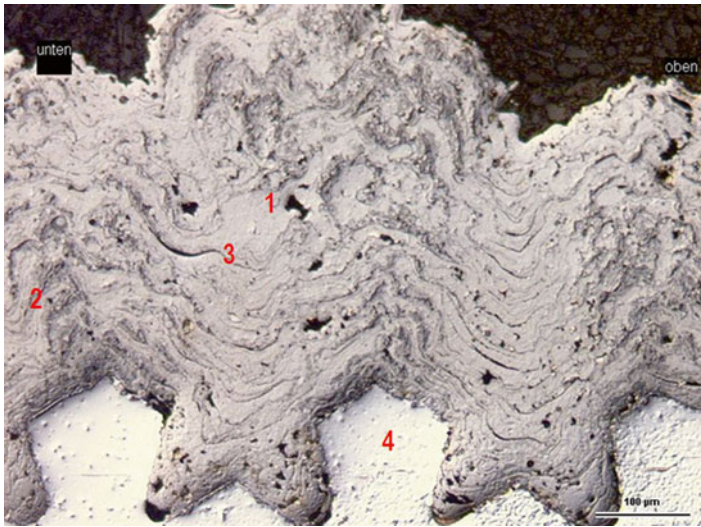


Fig. 8.1 Non-machined thermal-sprayed layer (PTWA method) with pores (1), oxide lamella (2), shrinking splits (3) and roughened substrate profile with undercuts (4)

As materials, iron wires with 0.3 % or 0.8 % C are approved in serial production in the meantime. These ferrous layers can be also generated under use of protective gas with a low oxide content of few vol.-% (volume percent) produced only. Without protecting gas, produced Fe coatings enclosed oxides of 15–20 vol.-%. Oxides in the Fe layer exist as wustite FeO , haematite Fe_2O_3 or magnesite Fe_3O_4 . The micro-hardness of the layer is approx. 300–600 $\text{HV}_{0.3}$ depending on the carbon content. It appears that there are further demands on increased corrosion resistance. Layers with very high chrome content made by pre-alloyed wires or filled tube wires are not yet generally accepted as their tribological properties are insufficient. For thermal powder coating methods, non-alloyable materials can be sprayed together. Therefore it is possible that also wear-resistant ceramic hard materials can be put into a corrosion-resistant matrix in order to fulfil the tribological and the chemical requirements.

As the thermal-sprayed layer is an inhomogeneous material, there is the intention to create a strong binding among of the single droplets. In practice it cannot be avoided that even with defensive machining parameters single melting particles are put out and so-called pull-outs are caused. This happens when the cutting force of the diamond grit is bigger than the cohesive strength of the layer. Then a non-disturbed cut of the diamond grits of the honing stone through the proper material cannot be carried out (Fig. 8.2).

The coated layer and the roughening method are to be laid out accordingly that the adhesion between layer and substratum is bigger than the cohesion within the layer. Having such conditions, the layer can be well machined without any risk that the cutting forces will remove single droplets or extensive large-scaled layer sections.

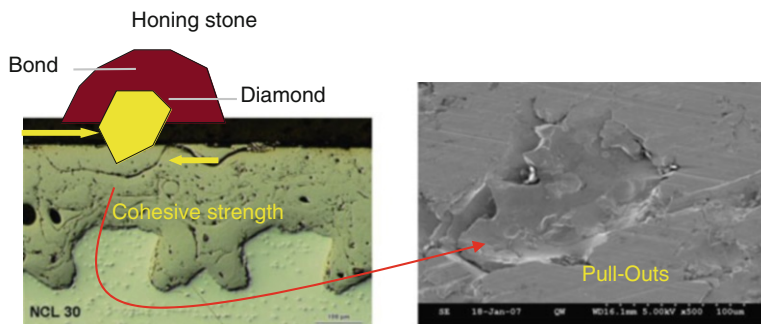


Fig. 8.2 Effect of cutting force in case of insufficient cohesive strength

If a layer withstands the conditions of the honing process, then there is a very low risk that the layer will be detached during operation as the machining forces are much higher than the shearing forces of the piston ring friction during the fired running of the engine. Bond strengths of at least 30 MPa are required as minimum condition. They are achieved by various procedures of the pretreatment.

8.3 Machining Task

As already mentioned, the thermal coating of cylinder bores is initially a process step by which a compound material as protective surface layer is put into the bore. The macroform of the substratum is not really an equidistant reproduction on the layer surface which is largely prevented by high roughness, pads on the bore edges or other material artefacts as local uneven layer thicknesses. The profiling of a functional surface is not the first goal and ability of a coating method but rather the task of the following machining process.

Principally the machining task is to achieve a designed smooth and functional surface starting with the rough sprayed layer surface of a cylinder bore. For this reason numerous quality parameters are defined and tolerated according to their function. The finished condition of the cylinder bore has to meet the functional requirements with diameter, roughness as well as form and position tolerances. Furthermore machining times as short as possible are demanded which can be realized by robust cutting parameters with high stock removal rates only. All following indicated tolerances are approximate values which can be achieved reliably in serial production. However, in individual cases the engine-specific requirements are to be considered which can lead to other than the given tolerance ranges.

In order to get functionally coated cylinder bores, the macroform size and cylindricity is primarily described with suitable measured tolerance values. The accuracies of the direction and position of the bore are defined by the quality values' rectangularity and position accuracy. As form tolerances the cylindricity and if applicable also roundness and straightness are used. Regarding dimensional

Feature	Approximate Tolerance
<i>Makro form</i>	
Rectangularity	ca. 0,050 mm for bore length
Position	+/- 0,1 mm
Cylindricity	$\leq 10 \mu\text{m}$
Diameter	ca. +/- 0,010 mm
<i>Mikro form</i>	
Reduced peak height R_{pk}	$\leq 0,25 \mu\text{m}$
Average roughness R_z	ca. $5 \mu\text{m}$
Cross hatch	ca. 30°
<i>Layer parameter</i>	
Porosity	2 – 6 % of considered face (PTWA)

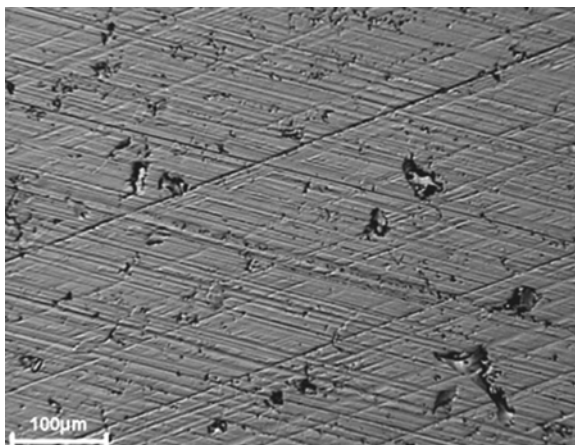
Fig. 8.3 Quality features with approximate tolerances

accuracy, there is no difference between a coated bore and a conventional cylinder bore of cast iron or aluminium silicon compound material. The microform of a coated bore described the topographical surface parameters. They are not only given by finish honing process but also by inhomogeneities immanent to the layer-like pores and pull-outs. In Fig. 8.3 the relevant quality features for the function including their respective approximate tolerances are summarized. They are based on the experience with passenger car engines. For coated cylinder bore liners of utility and marine engines of bigger sizes, there are no generally applicable indications.

The indication of the rectangularity is valid not only in the direction of the crank bore axis but also crosswise to it. Dependent on the function, it can be possible to specify a smaller tolerance range in axial direction and a wider one crosswise to it. The bore axis position is independent of the direction. Concerning the topographic parameter, only the reduced peak height R_{pk} and the cross-hatch are determined by finish honing. The R_{pk} value delivers the microcontact topography of the layer to the piston. This contact surface should be as smooth as possible so that the percentage contact area consists of the biggest possible number of contact points and reduces the slide friction hereby. However, for Diesel engines a R_{pk} value can be advantageous to increase the oil retention volume also in the honed profile elements by R_{pk} values up to $0.30 \mu\text{m}$. Furthermore the roughness of the bearing contact profile is to be considerably smaller than the depth of the opened pores in order to support the function of the pores as micropressure chambers for the hydrodynamic lubrication. The mean roughness depth R_z or also other measured values like core roughness depth R_k or the reduced groove depth R_{vk} are mostly dependent on the inhomogeneity of the layer structure.

Besides the quantitative evaluation of the macro- and microforms, there are further requirements with regard to the topographic structure quality. The still remained visible honing grooves are to be continuously cut. The smaller the honed roughness of the thermal-sprayed layer is, the smaller the oil retention volume of the honed topography. A flat cross-hatch of 30° is favourable for the formation of the hydrodynamic lubrication. At the edges of the pores, as less as possible, material like burrs and folded material is to go into the cavities and close these consequently [2].

Fig. 8.4 Finish-honed surface of a PTWA layer with pores, honing grooves and pull-outs



The pores and pull-outs are to be cut regularly on their edges and completely opened without any burrs. Finally a minimum of plastic deformation on the subsurface zone is to be achieved by low machining forces (Fig. 8.4). In addition it is required that beneath the surface, the layer structure is non-deformed as far as possible and the subsurface zone damage is minimized.

The material removal by honing in several steps can vary significantly as per coating process and the specific layer parameters. The layer thickness of APS layers is approx. 0.200 mm [3] and of PTWA and LDS layers 0.300–0.600 mm [4]. The remaining layer thickness of the finished bore is 0.080–0.150 mm. The stock removal ranges for honing and the number of honing operations are different accordingly. The stock removal for honing is approx. 0.200–0.500 mm on diameter. The cycle time for machining of thermal-coated cylinder bores in passenger car cylinder blocks is approx. 30 s. For cylinder liners of big engines and for stationary engines or marine engines, the machining times can be even up to some minutes.

8.4 Process Layout

For the machining of thermal-coated bores, two process chains are developed essentially. One of the variants uses a rough honing process by removing the layer material in equidistant manner and without influencing the axial position of the bore. This results in a constant layer thickness along the complete bore. The rough honing is required in cases of low layer thickness and when a correction of the bore axis with minimal stock removal risks is to break through the layer locally. Therefore in case of thin APS layers, only rough honing can be done. The bore position accuracy has to show the end quality already before the coating process due to the thin layer thickness, so that the existing position and rectangularity qualities are maintained as far as possible.

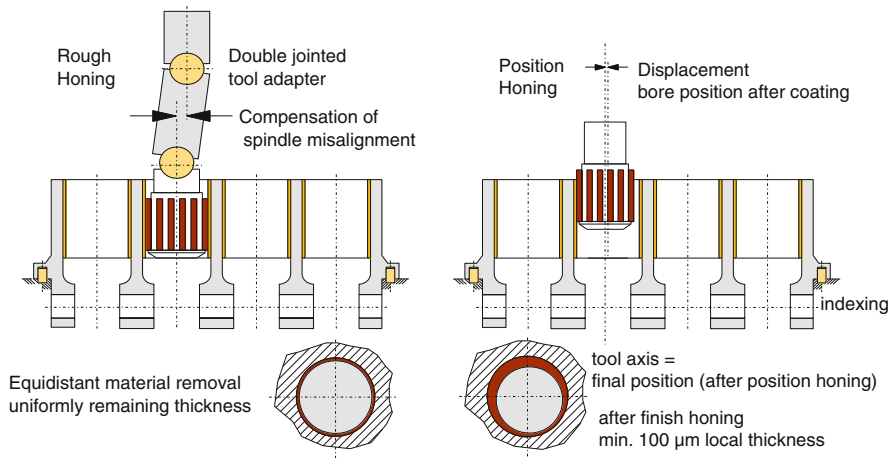


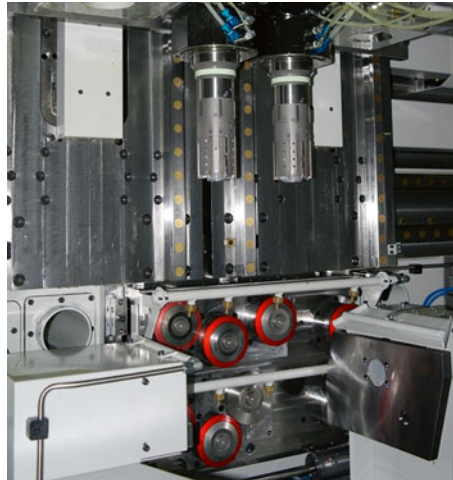
Fig. 8.5 Rough honing and position honing of thermal coatings

Fine boring as an alternative to rough or position honing was tested, but it is not introduced in serial production up to now. Tool life is low due to the abrasive effect of the layer oxides. Lifetime of cutting edges is less than 1/10 of tool life of honing shoes in position or rough honing process. The local cutting forces of fine boring inserts are higher than the honing forces. This can lead to layer deformation, particle pull-outs, microfissures and extensive layer damages in the subsurface zone. In addition very smooth surfaces are produced which make the cutting for the following honing tool more difficult. However, honing tools with relatively large working surface of the honing stones cause low local forces to the surface only so that subsurface zone deformation is of minor extent [5].

Figure 8.5 presents the different honing procedures for thermal-sprayed coatings. The rough honing tool follows the coated layer due to the flexible tool adaptation. There is no influence on the axis position of the bore. A constant layer thickness is generated.

While rough honing as a cutting intensive process is quite often applied for coated cast iron liners, steel tubes and thin APS coated cylinder bores, position honing is a new process which is already used in serial production in some cases. Particularly for thermal-sprayed layers being hard, but due to their lamellar material structure having good cutting conditions, position honing is a process with high cutting volume. Due to the suitable material conditions, low subsurface deformations and good position accuracies are achievable [6]. The demand for a position and rectangularity correction of the bore results in a different machining concept. In comparison with the conventional process, position honing needs a fixed axial tooling position which corresponds to the position and also the rectangularity of the finished axial bore position. When clamping the crank case, the position is defined by indexes which are related to the tooling axis [7].

Fig. 8.6 Machining station of a position honing machine with bend-proof tooling and clamping contours of workpiece adaption



During the position honing process, there is at the beginning a one-sided local cutting when the tool enters the bore. This restricted local stock removal is due to the position displacement between the bore and tooling axis. By increasing the stock removal during the cycle, machining covers finally the complete bore surface. When the machining of the total bore surface is achieved, then also position and rectangularity are given and now the tooling axis is identical with the bore axis. For this machining procedure high stock removals are necessary in order to get the best possible position correction. The remaining layer thickness of minimum 0.100 mm is to be respected. As an example, a layer thickness of 0.400 mm on a radius allows a theoretical correction of the position by 0.160 mm or of the eccentricity of 0.080 mm in case of a stock removal of 0.100–0.300 mm on a radius, with a remaining layer thickness of minimum 0.100 mm. This considers the local radial minimum stock removal of approx. 0.100 mm required to remove the spray roughness and allows a further radial stock removal of approx. 0.040 mm after position honing.

Figure 8.6 shows in particular the constructive features of a position honing machine. The tooling is attached to the spindle in a rigid way. To realize the required bending stiffness, the tooling is laid out as short as possible. As the requirements of the machining spindle for the position honing process are significantly different from the conventional honing spindles, a spindle with increased stiffness and high revolution speed of more than 2,000 1/min is applied. Only by this condition the high stability along the complete drivetrain arrangement from the spindle to the tooling as well as the high stock removal rate and position accuracy are enabled. The crank cases are positioned at adjusted indexing points of the horizontal or vertical clamping device. There are also clamping contours on the workpiece. The two spindle layout of the machine is not due to the process technology, but it offers the possibility to shift the workpiece. Thus the simultaneous machining of two bores is given.

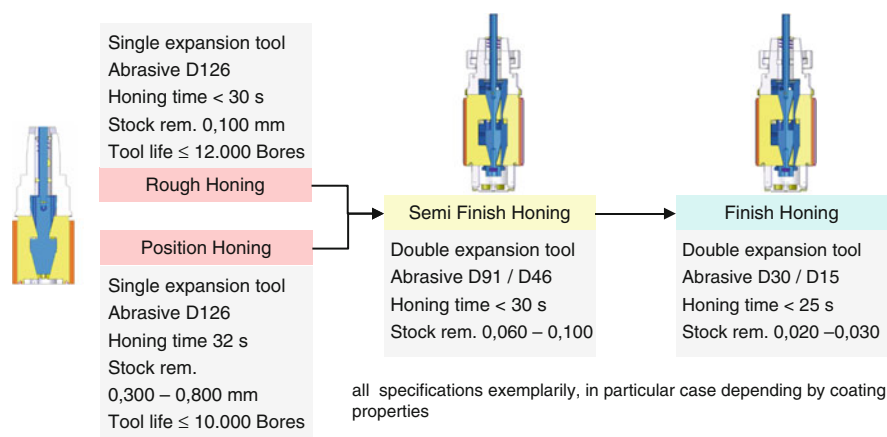


Fig. 8.7 Process chain for honing of thermal-sprayed layers

It can be mentioned that a pneumatic measuring system for size control is in serial application despite the high stock removal of up to 0.700 mm on diameter. The air nozzles are arranged as usual in the tooling. The cutting intensive process requires the coolant supply through the spindle.

The process chain up to the finished cylinder bore starts as presented in Fig. 8.7 with rough honing or position honing. In case of layer thicknesses of 0.200–0.300 mm, rough honing is recommended. Alternatively there is the position honing process which is more important for higher layer thicknesses. The cutting intensive process is done with a stock removal of up to 0.600 mm. It can be indicated that tool lifetimes of up to 10,000 bores for position honing are possible depending on the layer properties. This is an important advantage compared to fine boring of thermal-sprayed coatings. The following machining of semi-finishing and finishing is done with two spindles. Semi-finish honing and also the following finish honing operation work with double feeding system. They each have two sets of carriers with honing shoes which are activated successively. Four different abrasive grit sizes are necessary to improve step by step the roughness of position honing or rough honing of minimum $20 \mu\text{m } R_z$ up to finish roughness of approx. $5 \mu\text{m } R_z$ and R_{pk} value of $0.25 \mu\text{m}$. Only diamond shoes with microsplitting crystals and metallic-sintered bondings are in use. As usually hard material is embedded in the sprayed layer, the self-sharpening of the honing stones is given by the abrasive effect of the hard material particles. On the one side this effect assures the cutting quality of the abrasive stones, but on the other side, there are special arrangements to be taken to obtain economic tool life values.

The honing time is as mentioned before approx. 30 s. For the described process steps, the process chain requires at least three spindles, which have to be arranged for multiplication depending on the desired capacity.

The admissible process parameters like feeding pressure and cutting speeds highly depend on the cohesive and adhesive layer tensile strengths. In case of layer

structures having low cohesive strength, low feeding pressures and speeds are required. Otherwise the layer is pulled out locally and is detached in a lamellar manner. On the other hand there is experience with thick PTWA layers which can be machined with robust parameters due to high structure strength.

8.5 Machining Results

The size and geometry accuracies of thermal-sprayed bores correspond to the general values of cylinder bores and can be maintained reliably with the described process chain. By the taken measurements like increased stiffness of the drivetrain arrangement from spindle drive to position honing tool as well as the well-tolerated positioning of the workpiece by high-precision clamping contours, the position accuracies can be assured.

The indicated quality features in Fig. 8.3 are restricted significantly also for the position accuracy by the statistic tolerances. Thus, under favourable conditions, rectangularity values within the bore length even under 0.030 mm are realizable. In the same way the mentioned position accuracy can be reduced considerably. The photos of the surfaces presented in Fig. 8.8 are taken after position honing, semi-finish honing and finish honing.

After position honing (1) a highly fissured surface structure is shown which is characterized dominantly by cutting fissures. Furthermore on the surface there are clear material displacements visible, which also cause oversmeared material at the pores. The surface after finish honing (2) represents the functional topographic structure. The views of the polished section surfaces show fissures (1a) and pull-outs (1b) after position honing. A higher contact pressure of the honing stones is not allowed as it causes damage to the subsurface zone. After finish honing there is a smooth cut surface also with material out-pulls (2a) and pores in the subsurface zone just beneath the surface (2b) [8].

In Fig. 8.9 the particular topographic features of a finish-honed thermal-sprayed layer can be seen. The honing grooves are only slightly visible as the roughness is low. But they are evenly formed in both directions. The cut pores are visible as dark deepening. They can be distinguished clearly from the pull-outs which show at the cavity bottom a bright and molten smooth surface. Therefore it is concluded that attached melting particles are removed by honing. Crushed melting particles are visible slightly as material doublings or as folded material.

Optical surface measuring methods are getting more and more important in order to characterize honed surfaces of thermal coatings. At the first place, there is a three-dimensional detection of the topography compared to the tactile measuring systems often used up to now. In application white light interferometer and confocal measuring principles are used. This development supports the objectiveness of quality measuring [9]. Besides the 3D roughness value data, there is a further demand on information about porosity and separate oil retention volumes of pore

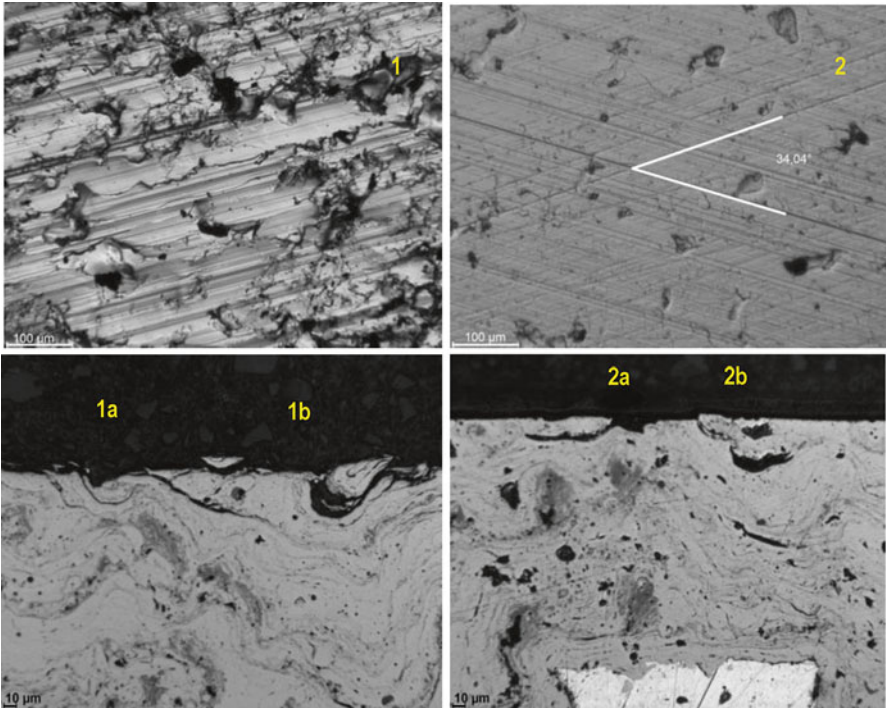


Fig. 8.8 Topographies and structure marginal zones after position honing and finish

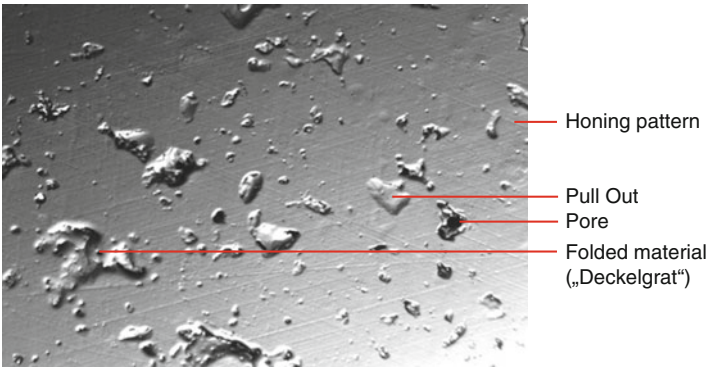


Fig. 8.9 Topographic features of a finish-honed layer surface (PTWA)

part and honed structure for thermal-sprayed layers [10]. The surface of Fig. 8.10 is taken by an optical confocal 3D measuring method. The measuring system consists of an angulated optical system and driven dipping guidance to access in axial and radial mode the measuring positions in the cylinder bore. Similar to the existing R_k values, roughness values of the surface are indicated like reduced peak height S_{pk} ,

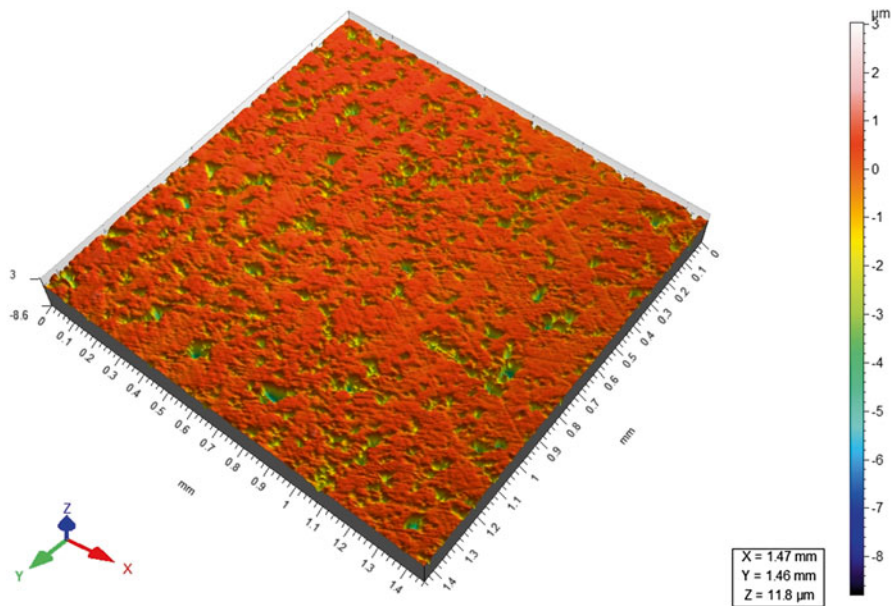


Fig. 8.10 3D optical presentation of topographic structures shown on an APS layer with fine honing grooves and approx. 8 % cavities (pores and pull-outs) $S_{pk}=0.12 \mu\text{m}$, $S_k=0.49 \mu\text{m}$, $S_{vk}=1.69 \mu\text{m}$ and $S_z=11.81 \mu\text{m}$ (Source: M. Jürgensen)

core roughness depth S_k and reduced profile depth S_{vk} . For equally honed cast iron surfaces, the differences between R - and S -values [11] are of minor importance. However, for a finish-honed porous surface of coated bores, the R - and S -values can be completely different, depending by the size and distribution of pores.

Figure 8.10 shows the topographic view of a finish-honed APS layer (atmospheric plasma spraying, Sulzer). The advantage compared with the cast iron surface consists in the porous structure. The surface of a thermal-sprayed coating contains cavities of only 8 % of the considered surface. In conventional plateau-honed cast iron, the comparable oil retention grooves however have three times higher part of the surface. However, the oil retention volume of both surfaces is in the same range, which means, thermal coatings have a comparable lubrication conditions but a more completed solid contact to the piston rings. Due to this the conditions of mixed friction are improved with profile characteristics of finish-honed thermal coatings. Additionally the pores as closed micropressure chambers will support the hydrodynamical friction which guides to less friction in lower range of rotational speed range [12].

With this topographical condition, at the beginning of fired engine running, a bearing surface is available. The pores are layered immanent features of the honed

surface structure. Also after advanced running duration with increasing wear of cylinder surface, new pores will always be opened, so that surface relief and its oil retention volume will not change essentially.

8.6 Summary

Machining of thermal-sprayed layers is a new challenge for new manufacture technologies, in particular for machining cylinder bores with different honing variants. New strategies for machine and tool layouts as well as in particular the availability of appropriate diamond stones considering the material-specific properties of the cutting process are essential.

Based on the coating material characteristics which are relevant for machining, a new honing process is presented. There are the material and mechanical properties and the layer structure. Following the general quality values and their functional tolerance ranges are described. Then the different variants of machining strategies are indicated, which are applicable for the different thermal-sprayed layers. The paper is closed by the discussion of the machining results regarding the functional properties, including by the evaluation of 3D surface measuring methods.

The answer to the public discussion of CO₂ reduction of combustion engines with minimized fuel consumption is reflected by numerous applications of thermal-sprayed layers with low friction used for cylinder bores. Honing of thermal-sprayed layers allows specific functional tribological surfaces with minimized friction. In general, this contribution to machining processes supports the sustainability of the combustion engine.

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Chapter 9

Coatings for Aluminum Die-Casting Dies

Sung Chul Cha

Abstract Aluminum die-casting dies are subject to severe loads, thermal softening, and shock as well as high-temperature wear and oxidation at temperatures exceeding 750 °C. Collectively, these decrease die's life cycle and increase production costs of aluminum parts. The objective of this work is to develop outstanding coating materials which can prolong the die's life cycle by more than 200 %. Specifically, in this study, we compared the critical properties (i.e., Al adhesion, thermal shock, stability, etc.) of 11 coatings, and subsequently, three best coatings are selected to be applied in production lines and evaluated for their overall performance and durability. The best performing coating TiAlCrSiCN is then characterized in terms of its nanolayered design, constituent elements, coating process, and effects. Especially, this and other newly developed coatings on conventional die material (SKD61) could be used as a substitute for more expensive high-temperature die materials.

Keywords Aluminum die-casting • Dies • Engine block • Transmission parts • Hard coatings • arc-PVD • TiAlN • AlCrN • CrTiAlN-CrON • TiAlCrN-CrON • TiAlCrSiCN • Adhesion test

9.1 Introduction

The current megatrend of automobile industries is to focus on novel “eco-friendly” technologies that can increase efficiency and productivity while at the same time reduce cost, emissions, and other harmful by-products. Current CO₂ emission of 130 g/km shall be reduced to 95 g/km prior to 2020 with enhancement of fuel economy by about 27 %. However, vehicle quality and safety, e.g., driving pleasure, vehicle size, and safety systems, interior design for overall comfort, audio, and navigation systems lead to significant weight increase. Therefore, all these works against the common goal of vehicle weight reduction are illustrated in Fig. 9.1. In order to achieve substantial increases in fuel economy, new and more effective

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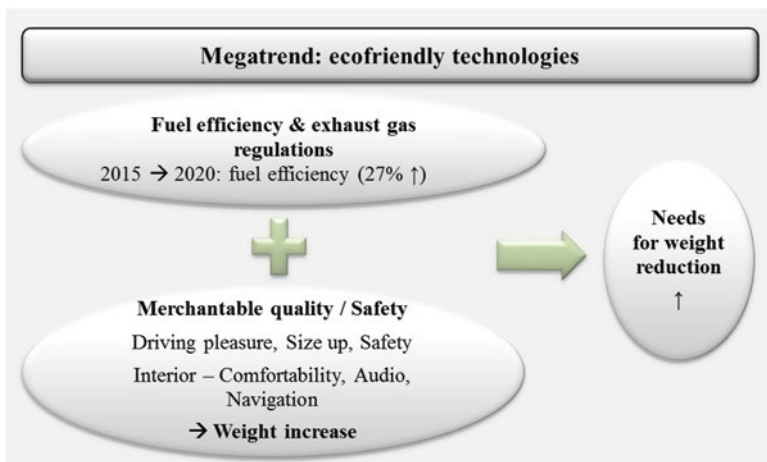


Fig. 9.1 Eco-friendly technologies and needs for weight reduction

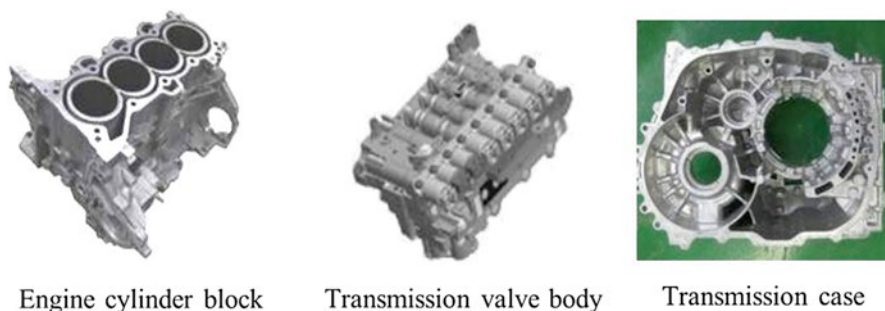


Fig. 9.2 Applied parts of Al die-casting

strategies have to be developed besides the friction reduction technologies that are being pursued at present; and one of the very obvious ones is to further reduce the weight of vehicles by all means. For this, most of the carmakers are currently concentrating on reducing weight through the use of more Al and advanced high-strength steels (AHSS). Al, which is the major material for weight reduction, is applied to engine cylinder block, transmission valve body, and case through Al die-casting process; see Fig. 9.2. An Al die-casting machine with representative drawings and actual dies used to make the engine blocks is shown in Fig. 9.3. These dies consist of moving and fixed parts, and die-casting process begins with inserting of cylinder liner to dies, and during die casting, both parts are together united. After die casting, the moving part is separated from the fixed part, and the engine block is picked up by the robot, and the cooling system cools both parts after the casting process.

One of the current problems of Al die-casting dies is short life cycle, e.g., the useful life of core pins and inserts is limited to about 3 weeks, and then they have to

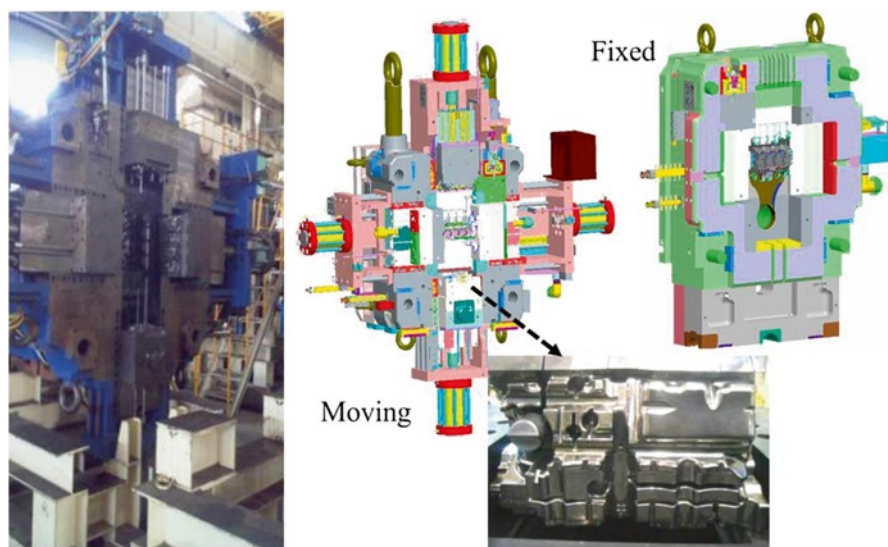


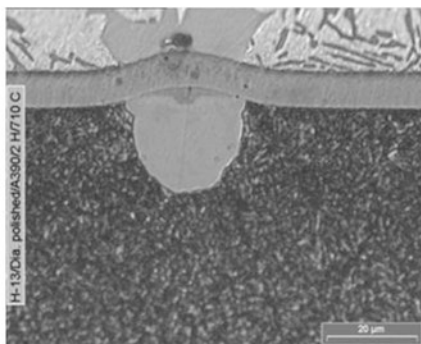
Fig. 9.3 Al die-casting dies for engine block production



Fig. 9.4 Damages on die surfaces – Al stuck, surface cracked

be replaced. Some of the reasons include molten Al adhesion and hence damage to die surfaces, which can lead to exterior problems on the cast parts with an error rate of 1.6 % (Fig. 9.4 shows examples of Al adhesion and buildup on a die surface). The life cycle of these dies is mainly influenced by the base die material, type of heat, and surface treatment used (including hardening and coating) besides die design and other process parameters. Furthermore, complex wear issues (due to corrosion, erosion, grinding, adhesion, abrasion) as well as heat-induced distortion and thermal shock from high processing temperature of max. 750 °C further aggravate the problem. Figure 9.5 shows the specifics of Al adhesion and soldering, leading to molten Al corrosion, where the effected region can be enlarged or further expanded by

Fig. 9.5 Al adhesion and soldering on die surface



Al adhesion / Soldering - molten Al corrosion
→ high temperature fatigue added

Die material (production 25t. shots)



SKD61- Heavily heat checked



HTCS135- good

Fig. 9.6 Die materials (SKD61, HTCS 135) after production of 25,000 shots

high-temperature fatigue processes leading to defective end products. Current die material is made of SKD61 with TiAlN coating on the surface. In Europe, high-temperature high-strength steels with high cooling capacity, e.g., HTCS 135 (Rovalma, SA) with TiAlN/AlCrN coatings, are also used for die-casting dies. It is reported that after 25,000 shots of production, HTCS 135 steel still has a good condition, as opposed to SKD61 which is heavily heat checked (see Fig. 9.6), but the price of HTCS 135 material is enormously high.

Current coatings for Al die-casting dies are mostly made of TiAlN and AlCrN; TiAlN is not thermally resistant enough, i.e., its hardness decreased after exposure at 750 °C. AlCrN coating is highly thermally resistant, but its adhesion resistance to Al is low (main element of coating, Al, has strong affinity to Al from Al bath). In Europe, new coatings are still in development (CrSiN) or partly applied (TiBN), but without significant improvements over the existing coatings.

9.2 Concept of New Coatings for Applications in Die-Casting Dies

The objective of this work was to develop low-cost material with new coating for solving the lifetime and quality problems in conventional die materials. Required properties of coatings except for fatigue, wear resistance, and low friction are high thermal resistance and anti-sticking property. These complex properties are required simultaneously: Bonding strength, stability at high temperature, low friction, wear, sticking (adhesion), and thermal resistances are affecting one another as can be seen in Fig. 9.7.

Hard TiAlN coating was developed back in 1986 for tools in high-speed machining and cutting applications. To increase the performance, a 4th element (from Cr, Y, V, Zr, Nb, Si) was added, which helped increase hardness and reduce grain size, and lead to the formation of highly protective and stable oxides at high temperatures. Particularly, it is reported that the addition of Si could increase the hardness and thermal and corrosion resistance and decrease the grain size to nanoscale as well. Moreover, SiO₂ formed at high temperature worked as TBC (thermal barrier coating), preventing further corrosion and oxidation. TiAlCrSiN coating is proven to be useful up to 1,000 °C and provided good performance in high-temperature applications [1–6]. Si was also used to improve the thermal and adhesion resistance of DLC (diamond-like carbon). Si-doped DLC also provided low surface energy to alter the wetting characteristics of coated parts.

TiAlCrCN coating for AHSS forming dies was developed by adding 10–20 at.-% carbon to improve anti-stiction and low friction behaviors. To further improve thermal resistance, Ti, Al, and Cr are often used with TiAlN and CrN coatings in a nanolayered fashion. As a result, the toughness and hence the impact resistance are improved substantially, resulting in further enhancement of wear reduction and life cycle extension [7]. To develop new coatings with 200 % durability, enhancement

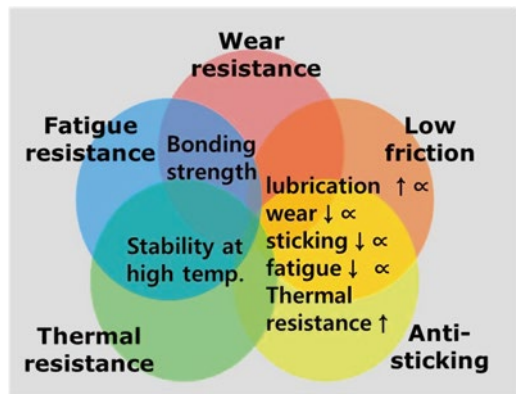


Fig. 9.7 Required properties and their relations for Al die-casting application

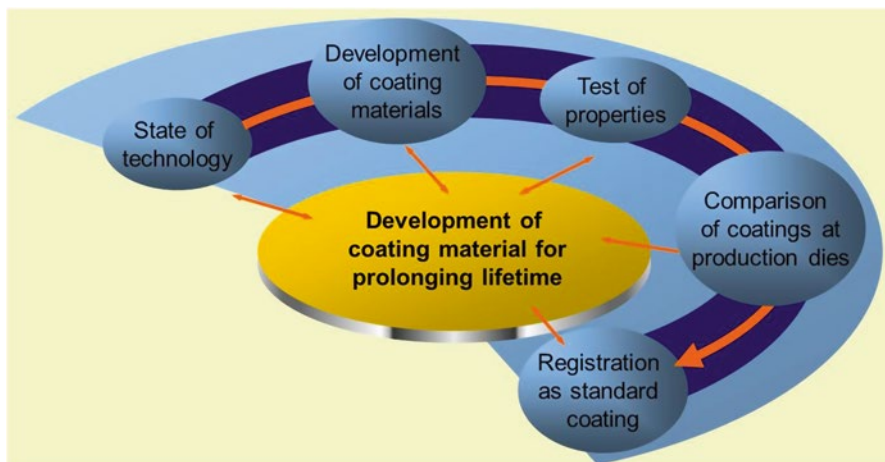


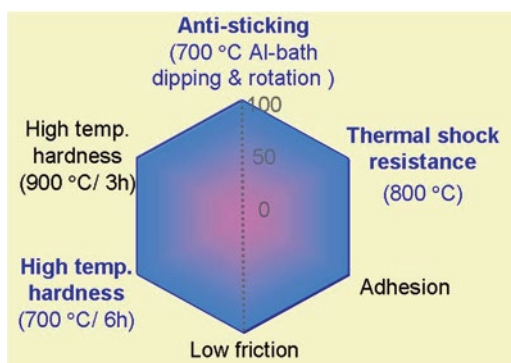
Fig. 9.8 Development process

over a current die coating like TiAlN was the aim of this work. The development process is composed of five steps: investigation of current state of the art, development of novel coating materials, test of properties, comparison of performance in production dies, and registration of standard coating as the final step as illustrated in Fig. 9.8. First two steps are described in the Introduction, and the last three steps are explained in next chapters.

9.3 Experimental

Typical steel used in the making of Al die-casting dies, i.e., SKD61, is used for the performance tests. Samples are quenched and tempered, plasma nitrided, ground, and polished for typical surface roughness of $0.1\ \mu\text{m}$. To assure a fair comparison, all specimens are coated with $10\ \mu\text{m}$ -thick coatings with an arc-PVD process. Samples in the form of pins (diameter 8, height 150 mm) and coupons (diameter 10, height 30 mm) are prepared to verify the properties, e.g., sticking (adhesion) behavior and hardness at room temperature and after high-temperature exposure to check the high-temperature resistance, thermal shock, adhesion, and friction behavior as shown in Fig. 9.9. A total of 12 candidates including current coating and uncoated baseline are included in the test program. Various coatings tested were provided by the well-known coating companies (Balzers, Dongwoo, Ionbond) (Table 9.1).

To compare the adhesion or stiction behavior of coatings to molten Al, various methods are surveyed: especially, Oak Ridge Nat. Lab. (USA), University of Braunschweig (Germany), and Ionbond (Switzerland) tried dipping materials to be coated in Al bath or carried out dipping and wetting tests [8–11]. The coated samples in the form of pin are dipped in $700\ ^\circ\text{C}$ Al bath and rotated to reproduce an

Fig. 9.9 Tested properties of coatings**Table 9.1** Candidate coating materials

No.	Sample	Candidates	Institution
1	A	CrTiSiN-CrON	Ionbond
2	B	CrTiAlN-CrON	Ionbond
3	C	CrTiAlN	Ionbond
4	D	TiAlCrSiN-CrON	Dongwoo
5	E	TiAlCrN-CrON	Dongwoo
6	F	TiAlN (current)	Balzers
7	G	TiAlN mod	Balzers
8	H	AlCrN	Balzers
9	I	AlCrN mod	Balzers
10	J	TiAlCrSiN	Dongwoo
11	K	TiAlCrSiCN	Dongwoo
12	Z	Noncoating	–

erosive attack of molten Al simultaneously (condition: 40 mm dipping depth, 14 times/min rotation). After dipping and rotating from 6 until 27 h, Al stuck on pins is removed with 10 % NaOH at 100 °C, and then, holes on the surfaces are observed as depicted in Fig. 9.10.

To duplicate thermal shock attack of Al bath to coatings, samples in the form of coupon are heated four times at 800 °C for 2 min and then twice air- and water-cooled. Subsequently, the samples are observed visually, and hardness and changes in thickness were measured, Fig. 9.11. Measurement of coating properties is summarized in Table 9.2. The friction behavior of coatings is observed by plate on disk test (10 N, 500 m, SUJ2 pin, coating as disk, dry). Hardness is measured with micro-indenter (0.05 N, 0.7 μ m indenting depth), and adhesion of coatings is measured with scratch tester. In addition, the Daimler-Benz Rockwell C adhesion tester was applied to classify the HF grades using an optical microscope according to the amount of cracking (HF1, high; HF5, low adhesion). Coating thickness is determined by Calotester, which measures the diameters of worn crater into the substrate through a rotating hardened steel sphere with diamond paste. Furthermore, in order to check thermal resistance of coatings, samples are exposed to 700 °C for 6 h and 900 °C for 3 h.



Fig. 9.10 Dipping and rotating test in Al bath for comparison of adhesion behavior. (a) Coated pins dipped into Al bath before (*left*) and after (*right*). (b) Al stuck pins (*left*), after NaOH washed pins (*right*)

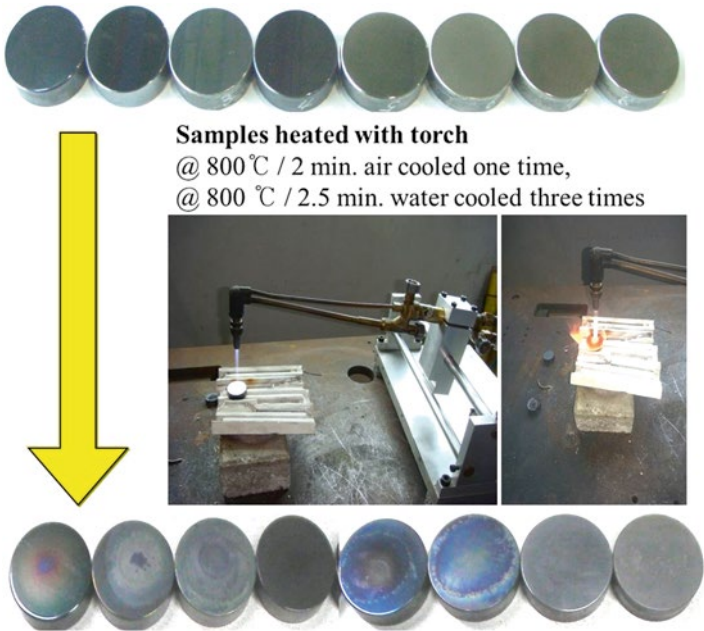
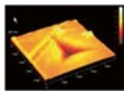
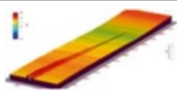
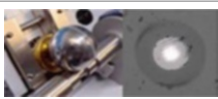


Fig. 9.11 Applied parts of Al die-casting

Table 9.2 Measurement of coating properties

Property	Equipment	Note
Friction wear	 Plate on disk	Condition: 10 N, 0.1 m/s, 2 km, dry Counterpart: AHSS disk (Ø6 mm, HV 365, Ra 0.5 µm) Thickness measurement by Calotester
Hardness	 Micro-indenter	0.05 N, 0.7 µm indenting depth
Adhesion	 Scratch tester	Diamond tip loading until first coating scaled off
Adhesion	 Rockwell tester	Cracking extent after pressing
Thickness	 Calotester	Worn crater with diamond paste
Temperature resistance	 Exposure chamber	Hardness comparison before and after 400 °C/3 h

9.4 Results

Table 9.3 shows the test results, comparing three best coatings over current TiAlN. Figure 9.12 illustrates those qualitative evaluations in spider diagrams. In particular, TiAlCrSiCN indicates excellent anti-adhesion performance and high thermal stability after exposure to high temperatures. Their thermal shock and friction behavior were within acceptable range.

Overall, TiAlCrSiCN, CrTiAlN-CrON, and TiAlCrN-CrON coatings showed excellent adhesion resistance, while their surfaces were rarely damaged after 27 h of dipping and rotating, compared to TiAlN with extensive damage on its surface, i.e., many holes on the surface, only after 6 h of dipping (see Fig. 9.13).

Competitive coatings for 700 °C Al die-casting dies shall be composed of more than three thermally resistant elements (Ti, Al, Cr) and tuned with adhesion-resistant Si/C or CrON layer. They could improve the adhesion resistance more than 450 % vs. current TiAlN coating.

Table 9.3 Results of properties (three best coatings vs. TiAlN)

		K	B	E	F
Coatings		TiAlCrSiCN	CrTiAlN-CrON	TiAlCrN-CrON	TiAlN
Anti-adhesion		+	+	0	–
Hardness (GPa)	RT	31.5	27.7	29.5	33.4
	700 °C	29.7	27.7	27.5	30.3
	900 °C	30.1	12.9	26.8	24.6
Thermal shock		+	+	+	–
Adhesion (N)		38	50	50	50
Low friction (friction coefficient)		0.47	0.53	0.57	0.43

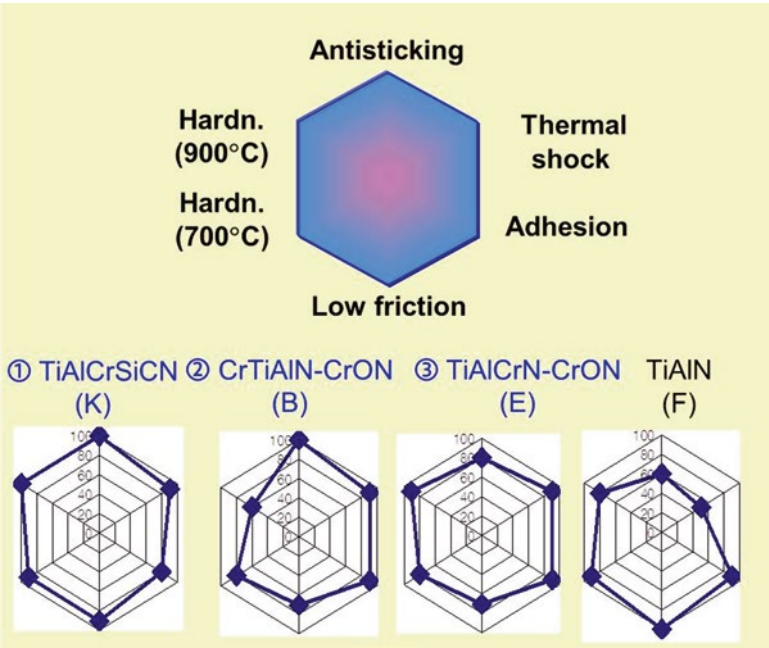


Fig. 9.12 Qualitative evaluation of coating properties—excellent coatings (K, B, E ranked), current TiAlN



Fig. 9.13 Images after adhesion test—excellent coatings (K, B, E ranked) after 27 h, TiAlN after 6 h, adhesion test

9.5 Discussion

TiAlCrSiCN coating is designed with three layers: (1) 4 μm CrN layer for bonding, reduction of residual stress, impact, and fatigue resistance; (2) 4 μm TiAlN/CrN nano-sized multilayer for high thermal, oxidation, and wear resistance and toughness; and (3) 2 μm TiAlN/CrSiCN nano-sized multilayer for adhesion resistance and low friction at high temperature as shown in Fig. 9.14.

TiAlCrSiCN is coated with Cr/CrSi/TiAl targets in a gas discharge plasma based on a gas mixture of Ar, N_2 , and C_2H_2 in the coating chamber under vacuum atmosphere. Figure 9.15 illustrates the target configuration and specific procedures used during deposition. Firstly, the chamber is heated up to 450 $^{\circ}\text{C}$ to evaporate most of the adsorbed species and contaminants from the chamber walls, an Ar ion plasma used to clean and activate the surfaces of test samples. In the beginning of the main

Fig. 9.14 TiAlCrSiCN coating layer design

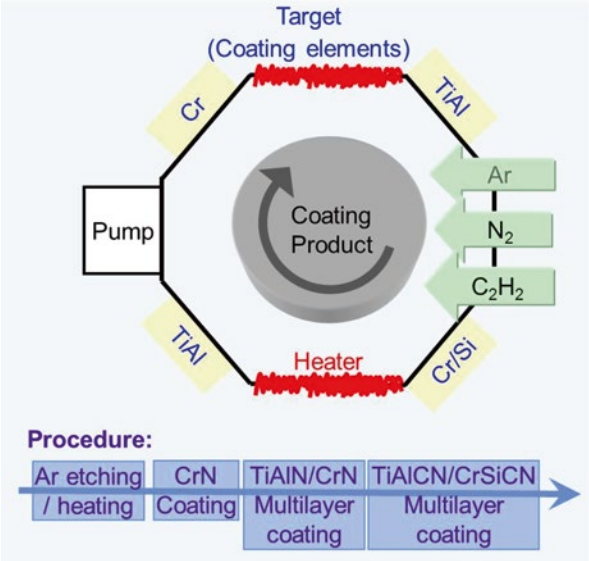
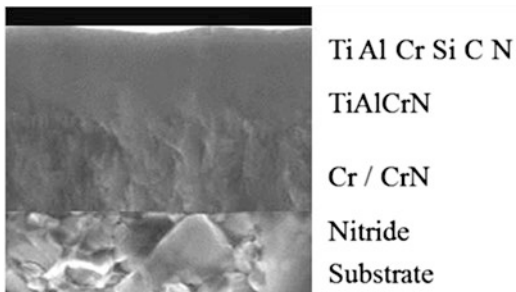


Fig. 9.15 Coating procedure of TiAlCrSiCN



Fig. 9.16 TiAlCrSiCN-coated Gamma engine block No. 3 die

coating process, CrN is formed with Cr target and N_2 gas and subsequently TiAlN/CrN multilayer with TiAl, Cr targets, and N_2 gas. Nanoscale multilayers are realized through symmetrical positioning of targets and rotating of coated parts at a desirable speed. Lastly, all targets and gases took part in the generation of nanoscale multilayers of TiAlCN/CrSiCN. Si content is fixed at 10 at.-% and that of carbon, 10 at.-%. Below these ranges, adhesion and low friction properties were worsened, and above these ranges, other elements were proportionally decreased, reducing hardness and thermal resistance. The effect of new coating with minimum lifetime extension of 30 % and enhancement of productivity of 15 % is calculated. It is based on the one set die of average weight of two tons, resulting in cost reduction of 16,000 US dollars. Figure 9.16 illustrates Gamma engine block die No. 3 coated with TiAlCrSiCN, and it is now in production.

9.6 Conclusions

To solve the adhesion problems and prolong the lifetime of Al die-casting dies, a total of eleven coatings are tested and compared with each other. As a result, three excellent coatings were found. Furthermore, it was found that a good die coating shall have three elements (Ti, Al, Cr) at minimum providing high-temperature resistance and good resistance to adhesion being provided by Si/C or CrON. TiAlCrSiCN, the best performer, shows excellent resistance to Al adhesion and has good high-temperature properties.

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Chapter 10

Coatings for Forming Dies of Advanced High-Strength Steel

Sung Chul Cha

Abstract Recently, most of the automobile companies and related industry increased their efforts in further increasing the safety and in reducing the weight of car body and chassis parts by using advanced high-strength steel sheets. Traditional hard coatings used in forming dies cannot fulfill the required wear resistance and durability. The coatings for the 980 MPa class forming dies need to have complex material performance like wear, temperature, and fatigue resistance as well as low-friction behavior. In order to develop the newer and higher-performance coatings for such forming operations, the ideas of carbon doping or carbon overlay coating should be considered for low-friction behavior in current dies. Furthermore, toughness, fatigue resistance, and strong bonding properties should be further improved through nitriding and followed up with multilayers of CrN, TiN, etc. In this work, TiAlCrCN and AlTiCrN + CN showed high promise among 18 coatings considered, and these should be considered for use on future drawing dies. Ultimately, the enhanced coatings or layer design with much refined nanograins and nanolayers can be developed for applications requiring the forming of much higher-strength steels (i.e., ultrahigh-strength steels or 3rd generation AHSS sheets) and of more complicated shapes.

Keywords Advanced high-strength steel • Car body parts • Chassis parts • Forming • Drawing • Die coatings • AlTiCrN+MoS₂ • AlTiCrN+CN • TiAlCrCN

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10.1 Introduction

One of the current megatrends in automotive industries is to focus on more “eco-friendly” technologies. In particular, the key objective of these industries in recent years has been to achieve a competitive edge in terms of fuel efficiency and exhaust gas regulations. Until 2015, the vehicle weight reduction of at least 10 % has been an absolute obligation in order to improve fuel efficiency and fulfill environmental regulations and crashworthiness of vehicles as well. Current CO₂ emission of 130 g/km shall be further reduced to 95 g/km until 2020 with additional improvement of fuel economy by about 27 %. In order to achieve this goal, let alone friction reduction of moving automotive parts, further weight reductions will be needed as an important requirement as well. Regarding fuel efficiency, most carmakers concentrate on reducing weight through the use of more Al and advanced high-strength steels (AHSS), in addition to power train downsizing. The use of AHSS in car body and chassis parts is assuming increasingly prominent position for not only safety but also weight reduction of vehicle by most of automobile companies and related industry.

AHSS is defined as steels with higher than 590 MPa tensile strength and includes dual phase (DP), transformation-induced plasticity (TRIP), complex phase (CP), martensitic steels (MS), and press-hardened steel (PHS), as illustrated in Fig. 10.1 [1]. As a general trend, the application of AHSS sheets in vehicles increased steadily over the last decade and currently stands at more than 50 % [2] as shown in Fig. 10.2.

Typical parts of AHSS are the reinforced center pillar outer/inner, the door impact beam, the roof rail, the reinforced roof side outer, the side sill outer, and the bumper back beam (Fig. 10.3), which are desired for superior crashworthiness. The press forming process (Fig. 10.4) is composed of drawing, trimming, restriking,

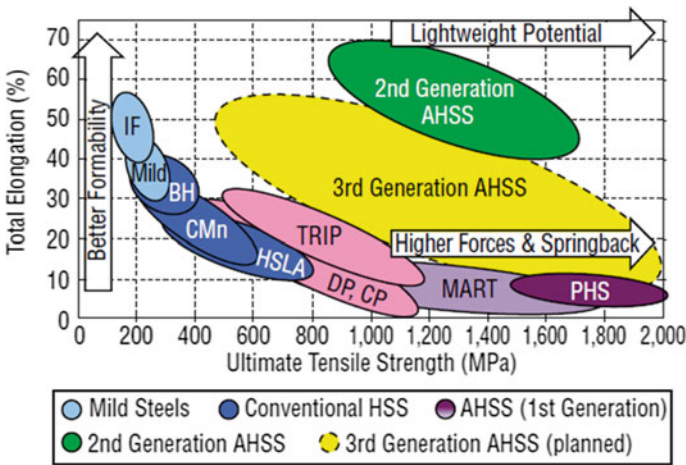


Fig. 10.1 Definition of AHSS steels [1]

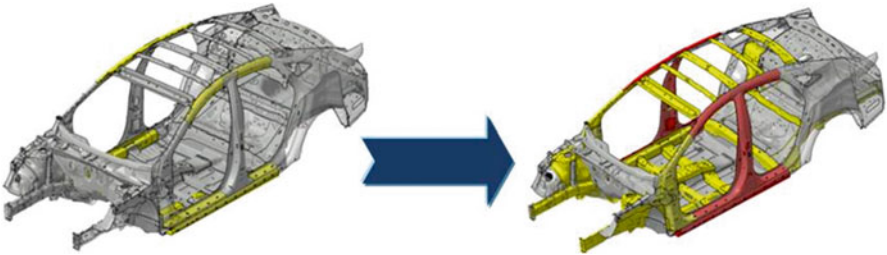


Fig. 10.2 General tendency and application rate of AHSS

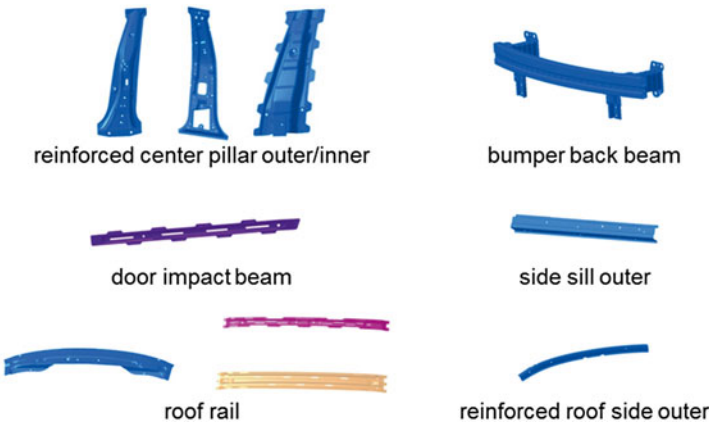


Fig. 10.3 Typical parts of AHSS

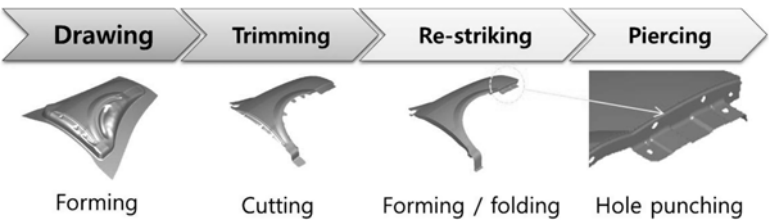


Fig. 10.4 Press forming process of AHSS

and piercing process. During drawing process, the spring back and twist problems are major concerns when forming AHSS. These can be solved with simulation, several trials, and correction of dies. Figure 10.5 shows the schematic and the actual image of a drawing die for center pillar outer as an example. The drawing die itself is composed of upper and lower dies, punch and blank holder. The upper die and middle of blank holder are heavily loaded during drawing process.

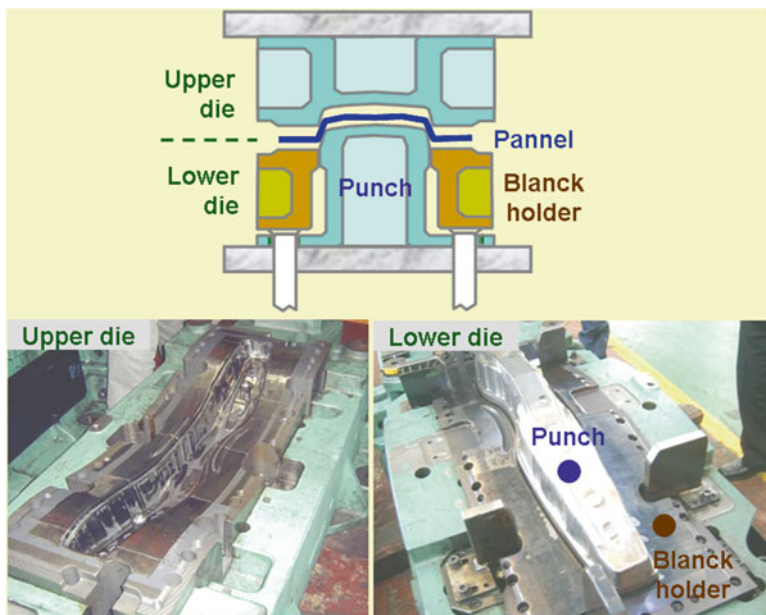


Fig. 10.5 Schematic and image of the drawing die [3]

Current drawing dies are heat-treated with thermal diffusion (TD) of vanadium carbide at 950–1,050 °C by dipping in salt bath to form a vanadium carbide layer with high hardness [3] or alternatively coated with TiAlN by PVD, but their wear resistance and durability are much shorter than the current requirement of at least 50,000 forming hits, e.g., for center pillar. After only 7,000 hits, the PVD TiAlN and other similar coatings are greatly worn off, and then, the formed work pieces are scratched and stuck to dies, and the dies themselves are worn off or cracked as well (Fig. 10.6). TD process provides longer wear life and acceptable surface finish up to about 30,000 hits after sizing correction. Furthermore, in the case of TiAlN, the coating cannot meet the minimum durability, so forming or drawing oils are used in order to reduce the friction and wear damage during forming. However, the use of oil can create other problems, e.g., oil can cause contamination for welding in subsequent processes [2]. In Europe, drawing dies are coated with TiC–TiN [4] by CVD at about 1,100 °C, and the base material is a powder metallurgical material, e.g., HWS Isotropic (Rovalma, SA, Spain). The rate of thermal deformation is high, and the number of reusing is limited due to the very high temperature of the coating process. In addition, the cost of drawing dies (inclusive of material and coating) is about US\$ 800,000, which is ten times more expensive than that of the ordinary dies [4]. Therefore, the development of more effective PVD coating process is strongly desired in the forming and drawing of automotive body parts (Fig. 10.7).

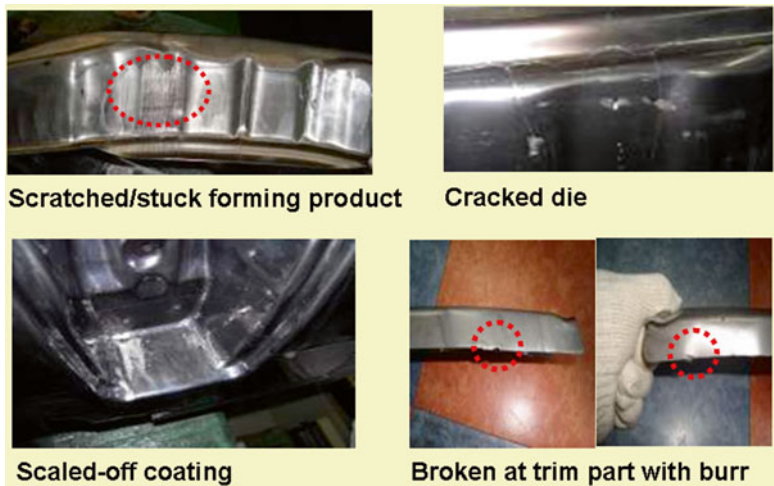


Fig. 10.6 Damages on formed products and drawing die [2]

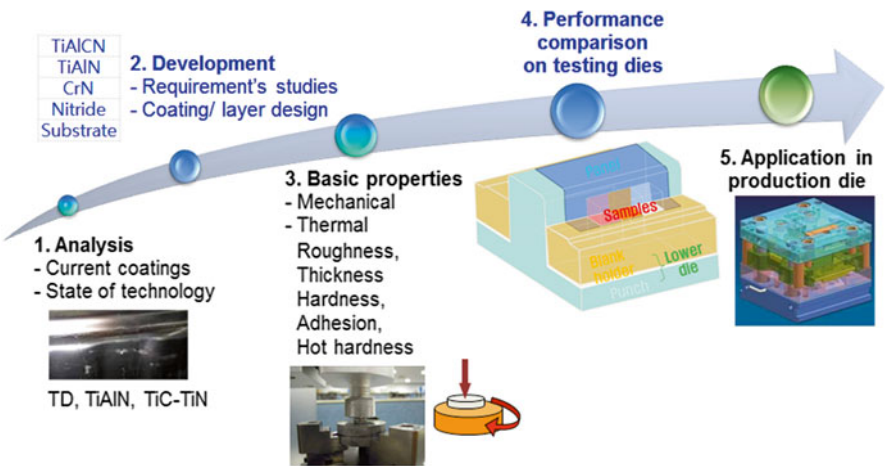


Fig. 10.7 Coating process development strategies for AHSS forming dies

10.2 Concept of New Coatings for Forming Dies

In general, the forming dies have diverse failure modes like gross cracking, plastic deformation, thermal shock, mechanical/thermal fatigue, and adhesive/abrasive wear [4, 6–8]. The various factors, e.g., material, design, heat treatment, surface condition, and coatings, must be appropriate for achieving long life in forming dies. For the kinds of tool steel, the use of proper heat treatment is essential for achieving higher hardness and toughness. The use of a nitride phase as underlayer plays an

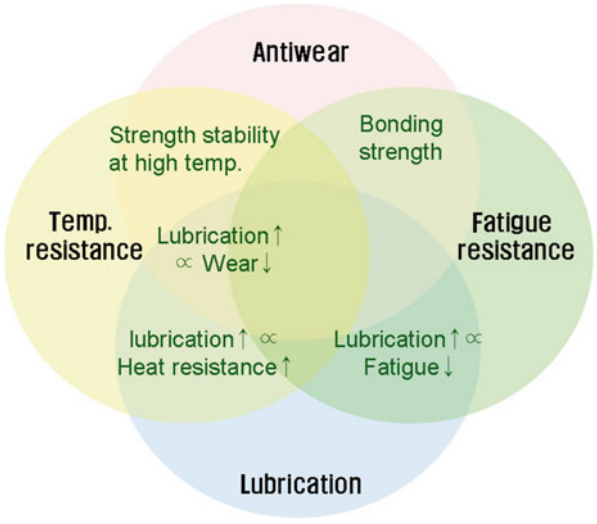


Fig. 10.8 Complex requirement for drawing die performance

Table 10.1 Typical requirements, surface engineering methods, and standard operating conditions for drawing dies in AHSS applications [4]

Requirement	Method/standard value
Antiwear	Hard nitride, carbide:
	TiAl-N, Al-Cr-N, V-C, TiCN, DLC (diamond-like carbon)
	Minimum 25 GPa, 4–6 μm thickness
Temp. resistance	Oxide former: Ti, Al, Cr, Si, V
	400 $^{\circ}\text{C}$ exposure, 80 % hardness at room temperature
Fatigue resistance	Plasma nitriding, buffer optimization
	Soft Ti/Cr, multi-/gradient layer
	Plasma nitriding minimum 80 μm
	Adhesion HF1-2 or minimum 30 N
Lubrication	Lubricated and anti-galling: C, Carbide
	Friction coefficient maximum 0.5 (against AHSS)

important role for attaining strong bonding, higher fatigue strength, and superior resistance to cyclic impacting and compression [9]. The coating as a top layer is needed for oxidation, anti-galling, and wear resistance. Especially the coatings for drawing dies are subject to a combination of complex wear, fatigue, and lubrication problems in addition to high-temperature exposure (i.e., as much as 400 $^{\circ}\text{C}$) as illustrated in Fig. 10.8.

These material properties can mainly influence the lifetime of drawing dies. The surface engineering methods and standard operating conditions for typical dies are summarized in Table 10.1.

10.3 Experimental

10.3.1 Tested Coating Materials

As the base metal forming dies, we used the conventional SKD11 (X153CrMoV12) steel and two new steel materials (DC53, DCMX, produced by Daido Steel Co.) in order to check the effect of base material composition on formability. DC53 and DCMX are characterized by their special chemical compositions, e.g., lower C and Cr and higher Si and Mo content to improve their fatigue resistance and toughness as well as to reduce the thermal deformation as summarized in Table 10.2. All specimens (diameter 37, thickness 15 mm) are heated at 1,020–1,100 °C with soaking time of 35 min for hardening and double tempering at 510 °C for 4 h to enhance their toughness, resulting in a minimum hardness value of 58 HRC [2]. Plasma nitriding is carried out at 460–490 °C for 8 h in a gas mixture that contained 15–20 % N₂, balance H₂, to produce the minimum thickness of 80 µm diffused nitride layer with Vickers hardness of 1,000 HV. Surface grinding and polishing with a requirement of minimum roughness value of Ra 0.1 µm were carried out before and after plasma nitriding and coating [4]. The main coating layer with the structure of single or multilayer is generated inclusive of the 0.5–2 µm-thick bonding layer, e.g., TiN and CrN. The minimum expected thickness of the coating layer was 5 µm in this work. Except for DLC by PVD sputtering, the coatings are coated by PVD arc method, Fig. 10.9.

Table 10.3 shows 15 new and modified coatings investigated in this study. In order to enhance the fatigue and friction behavior, the current coatings are optimized with respect to the thickness of the top layer. The new concept of coating design is to dope with the low-friction element like carbon and the low-friction top layer like DLC on the top of the heat-resistant elements.

10.3.2 Measurement of Coating Properties

The friction and wear behavior of coated test materials were investigated by a plate on disk test. Counterpart sample was 980 MPa AHSS disk (diameter 6 mm, HV 365, Ra 0.5 µm). Each experiment was conducted with a load of 10 N, rotating velocity of 0.1 m/s, and total length of 2 km in oil-free (dry) test conditions. The hardness of

Table 10.2 Chemical composition of die materials

Die materials for cold forming	Chemical composition (wt. %, max)								Hardness after heat treatment
	C	Si	Mn	P	S	Cr	Mo	V	
SKD11	1.40–1.60	0.40	0.6	0.03	0.03	11–13	0.8–1.2	0.2–0.5	HRC 58–62
DC53	1.0	1.0	0.4	–	–	8.0	2.0	0.3	HRC 62–64

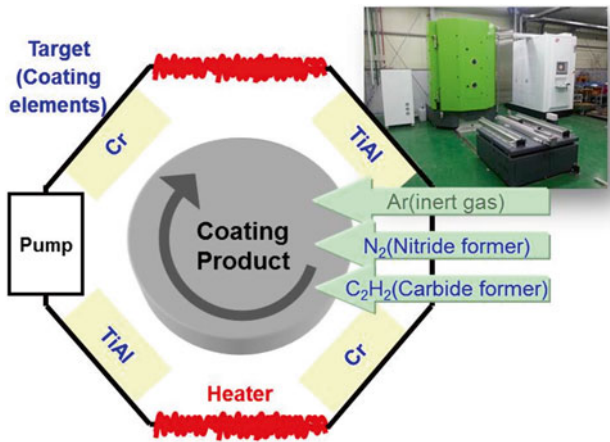


Fig. 10.9 PVD arc equipment (TiAlCrCN) with targets (TiAl, Cr) and gases (N₂, C₂H₂) at 450 °C

Table 10.3 Investigated new coatings and notes

New/ modified coatings	AlCrN, AlTiCrN+ MoS ₂ (normal/thick coated), CrN+ MoS ₂ , AlTiCrCN, AlTiCrN, CrTiN, AlCrN+ Si-DLC, AlTiCrN+ CN, CrON, TiC, TiCN, TiAlCrCN, DLC, TiAlCrN
Notes	
Procedure	(1) Quenching/tempering (2) Plasma nitriding (3) Coating (PVD arc, except for DLC by sputtering)
Requirement: Ra 0.1 μm, coating 5 μm, nitride layer 80 μm	
Institution: Balzers, Dongwoo, Ionbond, Platin	

coated samples was measured by microindenter with 0.05 N loading and indenting depth about 0.7 μm. The first scaled-off coating surface through critical load of diamond tip was measured by a scratch tester to determine the adhesion of the coating. In addition, the Rockwell C adhesion tester was applied to classify the HF grades using an optical microscope according to the amount of cracking (HF1, high; HF5, low adhesion). The thickness of coating is determined by Calotester, which measures the diameters of worn crater into the substrate through a rotating hardened steel sphere with diamond paste. The temperature stability and high-temperature resistance of test materials were determined by comparison of their hardness values before and after exposure to high temperatures. Exposure test is carried out at 400 °C for 3 h, and the hardness drop is determined. The special and sequential test protocol is summarized in Fig. 10.10.

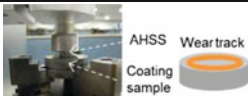
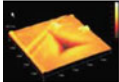
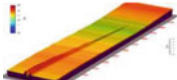
Property	Equipment	Note
Friction		Condition: 10 N, 0.1 m/s, 2 km, dry Counterpart: AHSS disc (Ø6 mm, HV 365, Ra 0.5 µm)
Wear	Plate on disc	Thickness measurement by calo tester
Hardness	 Micro-indenter	0.05 N, 0.7 µm indenting depth
Adhesion	 Scratch tester	Diamond tip loading until first coating scaled off
Adhesion	 Rockwell tester	Cracking amount after pressing
Thickness	 Rockwell tester	Worn crater with diamond paste
Temperature resistance	 Calo tester	Hardness comparison before and after 400 °C/3h
	Exposure chamber	

Fig. 10.10 Measurement of coating properties

10.4 Results and Discussion

The effect of different die materials, e.g., SKD11, DC53, and DCMX steel, was not considered in the measurement of basic properties. Therefore, the results are registered with an average and a range of data. Table 10.4 shows the results of coating properties in roughness, adhesion, bonding strength, hardness, thickness, and friction coefficient from the pin on disk wear test. Under consideration of complex coating properties, AlTiCrN + MoS₂, TiAlCrCN, DLC, AlTiCrN + CN, and AlCrSiN + CN coatings show high wear resistance, low friction, and high thermal stabilities. DLC is well known as a typical low-friction coating, but its thermal stability and environmental sensitivity are two major deficiencies. AlTiCrN + MoS₂ exhibits superior low-friction behavior that can be due to the good solid lubrication function of MoS₂ layer (which may be quickly removed because of low-temperature stability and moisture sensitivity during forming). Other coatings have the special layer design

Table 10.4 Coating properties of selected coatings (roughness Ra, adhesion HF, bonding N, friction coefficient, hardness GPa, thickness before and after plate on disk test)

Coating	Ra (μm)	Adhesion (HF)	Bonding (N)	Friction coefficient	Hardness (GPa)			Thickness (μm)—wear test	
					RT	400 °C	Δ (%)	Before	After
TD	0.07	3.3	31	0.73	26.5	22.4	15.5	11	10.8
TiAlN	0.03	1.2	48	0.72	33.5	30.5	8.9	5.3	4.4
AlTiCrN + MoS ₂	0.55	—	50	0.24	—	—	—	25	23.4
(MoS ₂ removed)	0.05	1.2	43	0.62	18	16.4	8.9	10.3	10.2
TiAlCrCN	0.07	1.2	49	0.42	28	27.6	1.5	5.2	4.7
DLC	0.03	1.2	48	0.27	28	27.6	1.5	4.4	4.3
AlTiCrN + CN	0.03	1.5	36	0.29	29	27.2	5.6	3.4	3.1
AlCrSiN + CN	0.02	1.5	37	0.28	27	25.8	3.4	2.9	2.8
AlTiCrN	0.04	1	24	0.56	38	29	23	3.6	3.4

which is composed of nitride, CrN, and main coating layer. Heat-resistant elements (Ti, Al, Cr) in combination with low-friction elements (C-doping, CN) have high hardness for wear protection as well as high-temperature resistance [5, 10].

TiAlCrCN shows a competitive result for AHSS application and is constructed of three coating layers (Fig. 10.11): (1) CrN layer for toughness and adhesion, (2) nano-sized multilayer of TiAlN and CrN with 30 nm thickness, and (3) TiAlCrCN as top layer. Zhang et al. [11, 12] investigated the effect of carbon and nitrogen content in TiAlCrCN on microstructure and determined that the variation of carbon content from 11 to 55 at. % changed the microstructure of coating, e.g., from crystalline, to polycrystalline, to nanocomposite, and then amorphous by increasing carbon content. Hardness is also changed from 1,200 to 2,400 HV at 25 at. % and then decreased to 1,200 HV at much higher carbon concentration. Friction coefficient was the lowest at 25 at. % carbon. Frequency of arcing influences the size of droplets on the coating surface, and usually low arc frequency leads to more formation of droplets with bigger sizes on the coating surface. Carbon is expected to decrease arc frequency and thus the formation of big droplets. On the contrary, carbon enhances low-friction behavior, but excessive carbon may lead to graphitization and thus reduction of hardness. Therefore, carbon content should be kept around 25 at. %.

Figure 10.12 shows the press machine with drawing dies that was used to test the performance of coatings while forming blanks or panels. In these experiments, two types of coated test pieces were used in the testing die. One piece was assembled in the upper die, and during drawing the bottom and side areas are contacted with the panel, and the other specimen is assembled into the blank holder, and during drawing the upper area is contacted with the forming panel. A total of three test series were carried out to compare the three current (TD, TiAlN, AlTiCrN+MoS₂) and six selected coatings (TiAlCN, TiAlCrCN, DLC, AlTiCrN, AlTiCrN+CN, AlTiSiN+CN). During these tests, the current TD coated samples are applied as a baseline for comparison. Drawing condition was 250 ton pressing, cushion pressure of 5 kgf/cm², RPM of 22–23, and 10,000 hits. Forming blank had a size of 350 by 296 by 1 mm and made from 980 MPa AHSS.

Figure 10.13 shows the surfaces of coatings after 10,000 hits of drawing operation. In the case of DLC coating, there are some evidences of surface damage like scratches and coating which appears to have been partially removed or scaled off. In the case of TiAlCrCN, there was no visible damage on the surface.

As part of a further optimization and coating development process, two other competitive coatings, e.g., TiAlCrCN and AlTiCrN+MoS₂, were applied on the production dies, which form the right-hand (RH) and left-hand (LH) center pillars with 980 MPa sheets (Fig. 10.14). As a result, these coatings achieved 2,500,000 shots and fulfilled the required wear resistance and durability of such forming operation.

Production dies are coated with TiAlCrCN (left) and AlTiCrN+MoS₂ (right) after 2,500,000 shots.

Fig. 10.11 Layer design, cross section, and top surface of TiAlCrCN

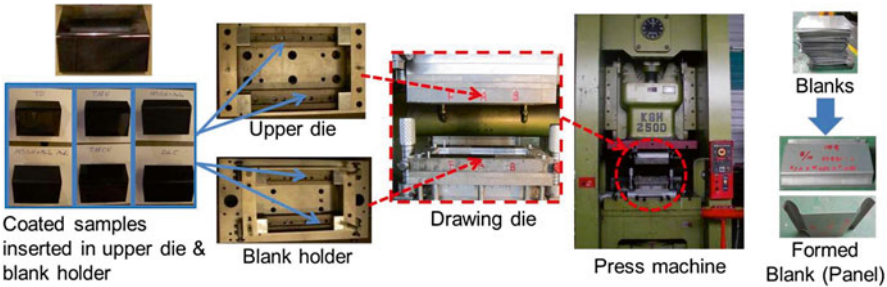
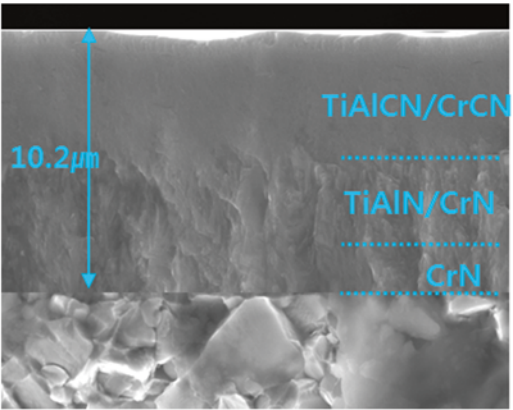


Fig. 10.12 Press machine with drawing dies together with coating samples and formed blank (DLC TiAlCrCN)

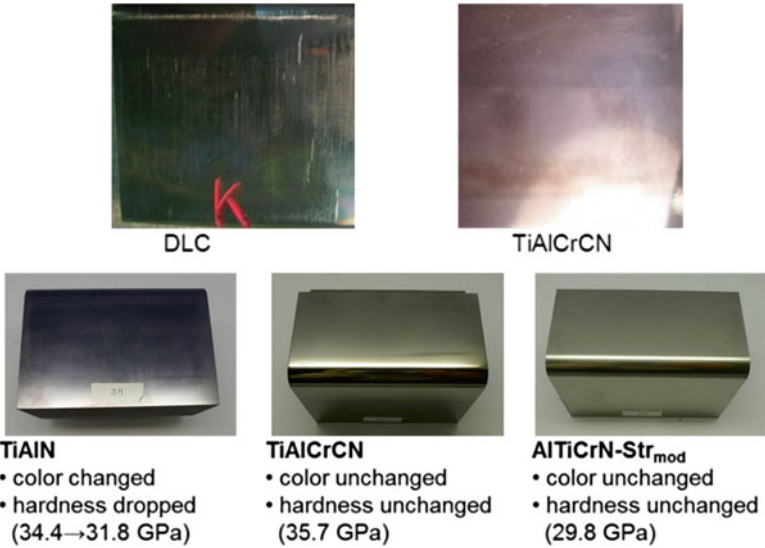


Fig. 10.13 Comparison of coatings with and without damages after 10,000 hits

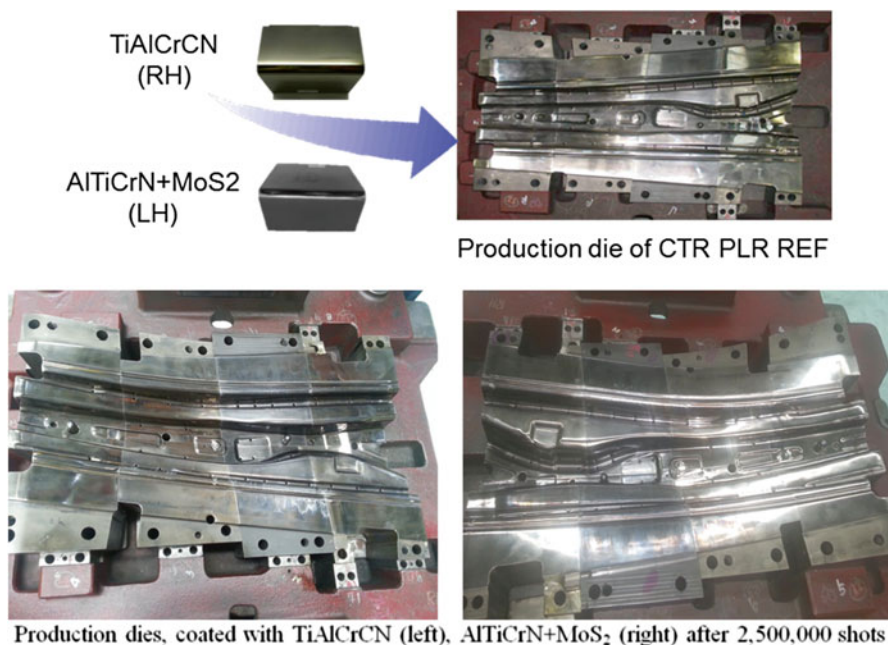


Fig. 10.14 Comparison and evaluation of two competitive coatings in production dies for 980 MPa center pillar (RH, TiAlCrCN; LH, AlTiCrN + MoS₂); images are taken after 2,500,000 hits or production shots

10.5 Summary and Future Work

Recently, most of the automobile companies and related industry increased their efforts in further increasing the safety and in reducing the weight of car body and chassis parts by using advanced high-strength steel sheets. Traditional hard coatings used in forming dies cannot fulfill the required wear resistance and durability. The coatings for the 980 MPa class forming dies need to have complex material performance like wear, temperature, and fatigue resistance as well as low-friction behavior. In order to develop the newer and higher-performance coatings for such forming operations, the ideas of carbon doping or carbon overlay coating should be considered for low-friction behavior in current dies. Furthermore, toughness, fatigue resistance, and strong bonding properties should be further improved through nitriding and followed up with multilayers of CrN, TiN, etc. In this work, TiAlCrCN and AlTiCrN+CN showed high promise among 18 coatings considered, and these should be considered for use on future drawing dies. Ultimately, the enhanced coatings or layer design with much refined nanograins and nanolayers can be developed for applications requiring the forming of much higher-strength steels (i.e., ultrahigh-strength steels or 3rd generation AHSS sheets) and of more complicated shapes.

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Chapter 11

Diamond-Like Carbon Coatings with Special Wettability for Automotive Applications

So Nagashima and Myoung-Woon Moon

Abstract Surface modification is an effective way of improving the tribological properties of base materials and is now actively being used in the automotive industry. Surface wettability can affect the overall performance of automotive components, such as windshields and mirrors, and controlling the surface hydrophobicity or hydrophilicity has been a major focus of research work in this industry. Diamond-like carbon (DLC), which is an amorphous carbon compound with outstanding mechanical and tribological properties, has gained considerable attention as a superior functional coating material and has been successfully applied to a range of mechanical automotive components, leading to better performance and durability. Recently, DLC-based materials with special wettability have been successfully used for the development of superhydrophobic and superhydrophilic surfaces, and a variety of industrial as well as biomedical applications have been proposed. Undoubtedly, being able to control the surface wettability using such DLC-based materials with tunable wettability would expand the original capabilities of the materials used in the automotive industry today. In this chapter, after giving a brief introduction to the fundamentals of surface wettability in relation to DLC coatings, we review recent studies on the control of surface wettability using DLC-based materials and then discuss future outlook.

Keywords Diamond-like carbon (DLC) • Surface wettability • Superhydrophobicity • Superhydrophilicity • Nanostructures • Nanopatterns • Thermal stability • Chemical vapor deposition (CVD)

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11.1 Introduction

Various materials, such as glasses, metals, polymers, and composite materials, are widely used in the automotive industry. These materials are expected to provide higher performance, longer-lasting excellent mechanical properties, better cost-effectiveness, superior safety, and reliability. However, they cannot always satisfy all of these requirements especially under severe environmental situations (e.g., heavy rain, snow, fog, and frost). When driving in the rain, for example, water drops adhering to the surface of windshields impair the visibility of drivers, which can affect the safety and comfort of the drivers.

Ensuring the safety and comfort of drivers irrespective of the weather conditions is a critical issue, and the surface wettability of materials plays a key role in determining their performance. As a consequence, the automotive glass industry has shown interest in imparting superhydrophobic and superhydrophilic properties to conventional windshields and mirrors. Some studies have focused on the effect of hydrophobic or hydrophilic treatment of windshields or mirrors on the performance and comfort of drivers [1–3]. Sayer et al. compared the visual performance of hydrophilic and hydrophobic coatings for rear windows and reported that the hydrophobic surface showed significant improvements, particularly when rated under dark conditions at night, whereas the hydrophilic coating did not show any significant improvement in the overall visual performance at a subjective level [3]. Today, various hydrophobic and hydrophilic coatings are readily available and are widely used. However, such coatings are not stable and only work as a temporary solution. Consequently, superhydrophobic or superhydrophilic surfaces that can endure extreme weather conditions and maintain long-lasting wettability are strongly desirable.

11.1.1 *Wettability*

Surface wettability is generally measured by the contact angle of a liquid droplet on a solid surface and has been extensively studied for various applications, including water harvesting, self-cleaning, antifogging, antibacterial, and cell culturing [4–7]. Superhydrophobicity or superhydrophilicity can be achieved by the combination of a hydrophobic or hydrophilic coating and micro-/nanoscale surface patterns. From a theoretical point of view, Wenzel [8] and Cassie and Baxter [9] laid the framework for understanding the role of surface roughness on wettability. Lotus leaves, for instance, are known for their superhydrophobic characteristics, called the “lotus effect.” When a water droplet is released onto a leaf surface, it forms a nearly perfect spherical shape, which rolls off and cleans the contaminated surface. This water-repellent behavior is attributed to the hierarchical structure and hydrophobic epicuticular wax crystalloids [10, 11]. Such superhydrophobic surfaces have been extensively explored for scientific and industrial applications [10, 12, 13] and have been developed using patterned micro-/nanostructures, such as carbon nanotubes,

zinc oxide (ZnO) nanowires, anodically oxidized aluminum, nanostructured polymers, and patterned steel [14–19]. For the fabrication of hydrophilic surfaces, several methods, including titanium dioxide (TiO₂) coating, surface modification through dry or wet etching, and ultraviolet/ozone treatment, have been suggested for various soft and hard materials. These methods are simple and significantly improve the wettability between water and solid surfaces. However, the short-term stability of the hydrophilic surfaces owing to the high surface energy has always been a major concern for practical applications.

11.1.2 Fundamentals of Diamond-Like Carbon

DLC is an amorphous carbon compound consisting of a mixture of sp^3 and sp^2 carbon bonds with various levels of hydrogen content. Since the first report by Aisenberg and Chabot in 1971 [20], DLC has received considerable attention as a functional material because of its outstanding properties, such as high hardness, low friction coefficient, high wear resistance, chemical inertness, and biological compatibility. DLC can be synthesized by various methods, such as chemical vapor deposition (CVD) and physical vapor deposition (PVD), and the precise control of the synthesis parameters directly affects the chemical nature of DLC, such as sp^3/sp^2 ratio and hydrogen content. Therefore, the properties of DLC can be controlled by changing the synthesis method and conditions.

DLC is the general term used for describing a broad range of amorphous carbon materials that can be categorized into several types according to their chemical nature and mechanical properties. Amorphous carbon (a-C) has a high content of sp^3 bonds (40–80 %), and hydrogenated amorphous carbon (a-C:H) contains less than 40 % sp^3 bonds [21]. Tetrahedral amorphous carbon (ta-C) is a type of a-C with a significant amount of sp^3 bonds (>70 %) [22]. Magnetron sputtering and cathodic arc evaporation are used for the synthesis of a-C, whereas plasma-enhanced chemical vapor deposition (PECVD) is commonly used for the deposition of a-C:H. The fraction of sp^3 bonds directly affects the mechanical properties, such as hardness, elastic modulus, and residual stress. The hardness of ta-C can be as high as 80 GPa and that of a-C:H is in the range 10–30 GPa [23]. Although the friction coefficient of a-C:H has been reported to be lower than that of ta-C in dry conditions, the wear rate of a-C:H is higher than that of ta-C in many testing conditions [24]. The residual stress in DLC is an intrinsic property and is strongly correlated with the kinetic energy of the deposited carbon atoms, which is dependent on the bias voltage, pressure, and precursor gas molecules [25]. When the stress exceeds the interfacial adhesion strength, delamination of the DLC coatings can occur, which eventually impairs the overall performance. In particular, the stress in ta-C is generally around 10 GPa [26] and delamination easily occurs. Lowering the residual stress by incorporating appropriate elements, such as Si and Ti, in the coatings and depositing interlayers onto the substrates prior to the DLC coatings are widely used methods to avoid delamination.

Several attempts have been made to further improve the properties of DLC and to overcome unfavorable situations, including interfacial delamination and film fracture. The amorphous nature of DLC allows for the incorporation of elements, such as Si [27–33] and F [34–36], and controlling their concentration is an effectively way of improving the mechanical and tribological properties of the coatings and lowering the severity of residual stress. For example, Choi et al. prepared Ag-incorporated DLC films with an ion beam deposition method and investigated the effect of the Ag content on the residual stress [37]. Their results showed that increasing the Ag content up to 9.7 at.% resulted in a decrease in the residual stress from over 3.0 to 1.3 GPa, indicating that the residual stress was highly dependent on the Ag content. Lee et al. synthesized ta-C films using a filtered vacuum arc of graphite with simultaneous sputtering of Si and measured the residual stress by varying the Si content [38]. They reported that the residual stress decreased from 6.0 to 3.3 GPa by incorporating 1 at.% Si, and further increase in the content to 50 at.% resulted in a decrease in the stress to 0.8 GPa.

Owing to their outstanding physical properties, DLC coatings have been effectively applied to automotive mechanical components, such as engine components, gears, piston rings, and bearings [39–42]. Recently, DLC-based materials with controlled wettability have also been used to fabricate superhydrophobic and superhydrophilic materials. An approach to controlling the surface wettability using DLC-based materials with special wettability would expand the original capabilities of the materials used today in the automotive industry. In the next section, we review recent studies on the control of surface wettability using DLC-based materials with special wettability.

11.2 Controlled Wettability Using DLC Coatings

11.2.1 *Development of Hydrophobic Surfaces Using DLC-Based Materials*

Chemical modification by the incorporation of a third element or compound, such as Si–O, Si, or F, into the amorphous carbon matrix has proven to be effective in decreasing the surface energy. DLC films synthesized from hexamethyldisiloxane (HMDSO, $\text{Si}(\text{CH}_3)_3\text{–O–Si}(\text{CH}_3)_3$), which are generally called SiO_x-DLC, SiO_x-C:H, or a-C:H:Si:O, are known to exhibit hydrophobic characteristics and have been effectively used as hydrophobic materials [17, 18, 43–47]. For example, Kim et al. synthesized a-C:H:Si:O film of about 10 nm in thickness from a mixture of hexamethyldisiloxane (HMDSO) and Ar by a radio-frequency (RF)-PECVD method. The static and dynamic contact angles were measured to be 101.8° and 12.6°, respectively [17]. Furthermore, hydrophobic films have been successfully deposited on patterned substrates to fabricate superhydrophobic surfaces. Rahmawan et al. reported a superhydrophobic surface consisting of a SiO_x-DLC film and micropillars of poly(dimethylsiloxane) (PDMS) [18]. The static contact angle of the film on a Si wafer was measured to be 106.4°. When the film was deposited on the

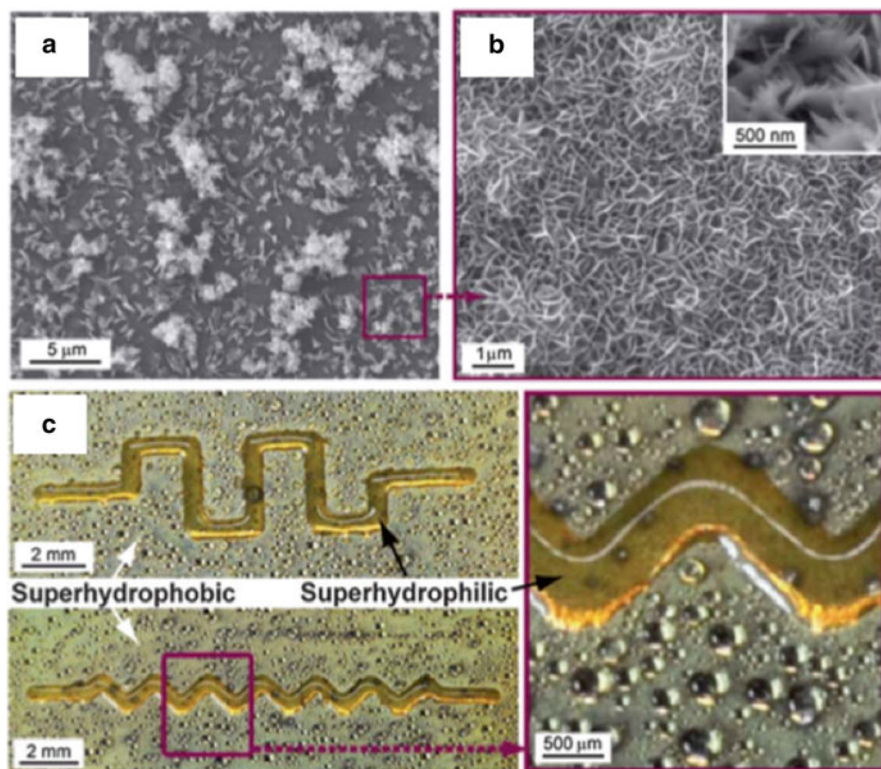


Fig. 11.1 Scanning electron microscopic (SEM) images of surface micro-/nanostructures on a steel sample with (a) low and (b) high magnification of steel (inset: magnified SEM image). (c) Optical microscopic images of superhydrophobic-/superhydrophilic-patterned steel masked by a microchannel after water condensation and a magnified image around a microchannel from the boxed area (bottom right) [44]. Reproduced with permission from The Royal Society of Chemistry

micropillars, nanoscale wrinkles were formed on the top of the pillars because of the residual compressive stress of the film (0.54 ± 0.01 GPa) and the difference in elastic moduli between the film (72.04 ± 3.68 GPa) and the substrate (~ 2 MPa), resulting in the formation of a dual-scale hierarchical structure. Because of the hydrophobic nature of the film and the hierarchical structure, the resulting surface showed superhydrophobicity with a static contact angle of above 160° and a contact angle hysteresis of 3° . Her et al. developed a superhydrophobic surface by combining a a-C:H:Si:O film and nanoflake or needle patterns of alloy steels (Fig. 11.1) [44]. The film deposited on various types of flat alloy steel substrates showed a static contact angle of $\sim 95^\circ$ and a contact angle hysteresis of 40° or above 90° . When the film was deposited on patterned substrates, which were prepared by CF_4 plasma treatment and subsequent water immersion of the alloy steels, the surface showed superhydrophobic characteristics with a wetting angle of above 160° and hysteresis of 10° . Her et al. also fabricated a superhydrophobic surface composed of a SiO_x -C:H film and nanopillars of poly(methyl methacrylate) (PMMA) (Fig. 11.2) [46].

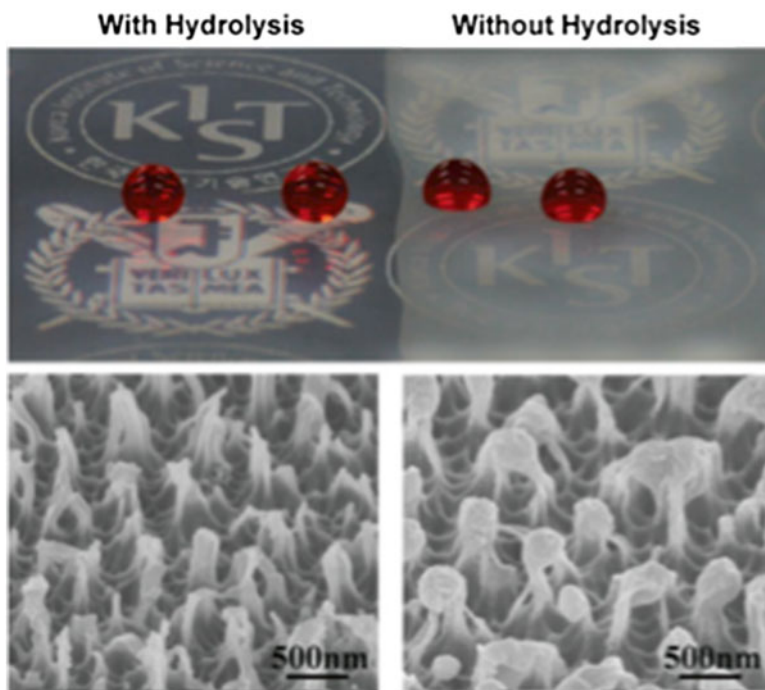


Fig. 11.2 Water droplets on hydrophobic surfaces made with (*left*) and without (*right*) water immersion and SEM images of the surfaces. Reprinted from ref. [46] with permission from John Wiley and Sons

While the static contact angle of the film on a flat PMMA substrate was 91° , that of the film deposited on nanopillars of PMMA induced by CF_4 plasma treatment and a subsequent hydrolysis process with water immersion was 159° . In addition, the contact angle hysteresis was measured to be as low as 3° , and the transmittance of the superhydrophobic surface measured by ultraviolet–visible spectroscopy was 95 %, indicating its excellent transparency. Ko et al. reported that deposition of $\text{SiO}_x\text{-C:H}$ film onto a carbon fiber network with hairlike nanostructures resulted in superhydrophobic properties [45]. The pristine carbon fiber network showed hydrophobicity because of its microscale fibrous structure, and the static contact angle and contact angle hysteresis were 147° and 71° , respectively. After deposition of the hydrophobic film onto the carbon fiber network, the static contact angle increased to 155° , while the contact angle hysteresis decreased to 20° . When the film was deposited on the carbon fiber network with nanoscale hairlike patterns induced by oxygen plasma treatment, the static contact angle increased to 160° and the contact angle hysteresis was less than 5° , demonstrating further enhanced superhydrophobicity. Cha et al. prepared a superhydrophobic surface by combining nanopillars grown on a Si wafer and a hydrophobic $\text{SiO}_x\text{-DLC}$ film and investigated the thermal stability [48]. The surface containing nanopillars with an aspect ratio (ratio of the height to the diameter of a nanopillar) greater than 5.2 showed a stable superhydrophobic nature

with a static contact angle of 155° at temperatures up to 350°C . However, when the temperature was further increased above 450°C , thermal degradation of the SiO_x -DLC film occurred and a transition from a Cassie–Baxter state to a Wenzel state was triggered, leading to an abrupt change of the wettability from superhydrophobic to superhydrophilic, where the contact angle decreased to less than 10° .

Surface fluorination using fluorocarbon plasma or incorporation of fluorine into the DLC films has been effectively used to make the surface of DLC-based materials hydrophobic [34–36, 49–51]. Roy et al. developed a hydrophobic surface by CF_4 plasma treatment of Si–DLC film [51]. The Si–DLC film with a Si concentration of 2 at.% was first prepared on a flat Si wafer and showed a contact angle of about 70° . The surface was then treated with CF_4 plasma, resulting in the formation of hydrophobic surface with a contact angle of greater than 90° . Hasebe et al. synthesized F-DLC films from a mixture of acetylene (C_2H_2) and hexafluoroethane (C_2F_6) gas with the RF-PECVD method and investigated the effect of the mixture ratio on the surface wettability [36]. The static contact angle varied in the range 65° – 91° depending on the mixture ratio, and the highest static contact angle was obtained when the partial pressure of C_2F_6 during the synthesis was 80 %. Hasebe et al. applied a highly hydrophobic F-DLC film to a patterned surface to develop a hydrophobic, lotus-leaf-like dual-rough surface [52]. The static contact angle of the F-DLC film on a flat Si wafer was about 84° , whereas for the film deposited on the dual-rough surface, the static contact angle was about 131° .

11.2.2 *Hydrophilic Surfaces Using DLC-Based Materials*

Hydrophilic and superhydrophilic surfaces have been actively studied for various applications, such as water harvesting, self-cleaning, and cell culturing [4–7]. Plasma treatment is considered to be a simple but effective method for fabricating highly hydrophilic surfaces, and oxygen plasma is commonly used for the surface treatment of DLC coatings. Nagashima et al. reported the effect of oxygen plasma treatment on the surface wettability of DLC film [53]. They deposited a DLC film of 50 nm in thickness on polycarbonate (PC) substrates from C_2H_2 gas using the RF-PECVD method. When the surface was treated with a low-power oxygen plasma, the surface became superhydrophilic with a static contact angle of about 11° . Roy et al. prepared a hydrophilic surface by oxygen plasma treatment of Si–DLC film [51]. The Si–DLC film with a Si concentration of 2 at.% prepared on a flat Si wafer had a contact angle of about 70° . When the surface was treated with oxygen plasma, the polar component of the surface energy decreased, lowering the contact angle to about 13° .

These methods are readily available and effective for enhancing the surface hydrophilicity. However, maintaining the long-term stability of such hydrophilic surfaces has been a big challenge for practical applications. Because of the relatively high surface energy, attachment of hydrocarbons to the surfaces as well as reorientation and migration of the polar functional groups introduced on the surfaces can easily occur, decreasing the surface energy and, in turn, decreasing the hydrophilicity. As a consequence, the hydrophilicity can only be maintained for a few days or

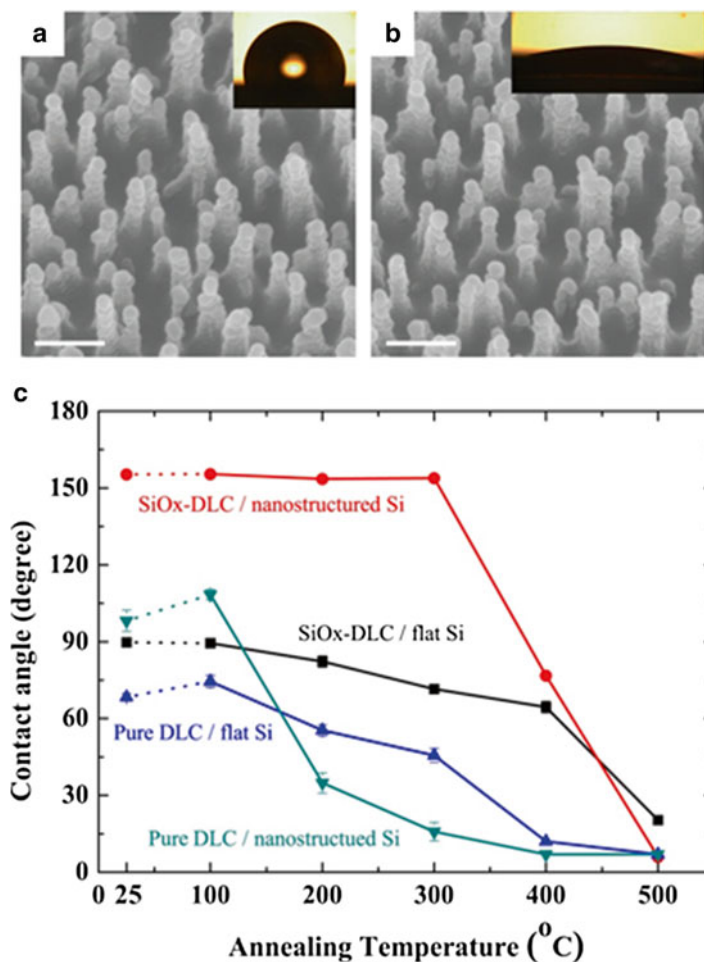


Fig. 11.3 SEM images of nanostructured Si wafers at (a) 100 °C and (b) 300 °C for the pure DLC coating (scale bars: 300 nm). (c) Water contact angles on nanostructured and flat surfaces coated with SiOx-DLC and pure DLC measured at several annealing temperatures. Reprinted from ref. [45] with permission from Elsevier

even a few hours. The development of long-lasting hydrophilic surfaces is strongly desired for a wide range of applications.

Yi et al. reported a long-lasting superhydrophilic surface prepared by oxygen plasma treatment of Si-DLC film [54]. The Si-DLC film was synthesized from a mixture of benzene and diluted silane ($\text{SiH}_4:\text{H}_2=10:90$) gases by the RF-PECVD method, and the surface was subsequently treated with oxygen plasma. With a Si fraction of about 1 at.%, the surface showed superhydrophilicity with a contact angle of about 10° , which lasted as long as 20 days in ambient conditions. They

attributed the long-lasting superhydrophilicity to nanostructures with a roughness of ~ 10 nm evolving on the surface because of the selective etching of the carbon matrix in the film by oxygen plasma and Si–O_x bond enrichment on top of the nanopatterns. This film has been successfully used as a coating material for the fabrication of superhydrophilic structured surfaces [55, 56]. Cha et al. reported that a surface consisting of nanopillars of Si (aspect ratio >5.2) combined with a hydrophobic SiO_x–DLC film showed superhydrophilicity when it was annealed above 450 °C (Fig. 11.3) [48]. Additionally, they mentioned that such Si nanopillars coated with SiO_x–DLC film exhibited superhydrophilicity regardless of the aspect ratio of the nanopillars when annealed above 450 °C.

11.3 Summary and Perspective

We have described the fundamentals of DLC coatings and discussed the control of the surface wettability of conventional materials using DLC-based coating materials. SiO_x–DLC films synthesized from HMDSO have effectively been used in combination with micro- or nanoscale structures, such as pillars and flakes, for the fabrication of superhydrophobic surfaces, which have static contact angles of around 160° and a contact angle hysteresis of about 10° or less. F-DLC films have also been actively deposited on flat and patterned substrates, including the lotus-leaf-like hierarchical structure, to enhance the surface hydrophobicity, showing the contact angles of around 150°. For the development of superhydrophilic surfaces, oxygen plasma treatment has been widely used owing to its simplicity and effectiveness. DLC and Si–DLC films treated with oxygen plasma show superhydrophilicity with static contact angles of around 10°. Moreover, the oxygen plasma-treated Si–DLC film maintains its superhydrophilicity for as long as 20 days in ambient conditions. Since long-lasting superhydrophilicity has always been an issue that needs to be addressed because of the aging effect, the superhydrophilic Si–DLC film can be regarded as a revolutionary material.

For automotive applications, not only the aforementioned special wettability but also other properties, such as low friction, wear resistance, sticking resistance, and high temperature stability, need to be guaranteed irrespective of the environmental conditions [57]. Thermal stability is an important property, and there have been reports of hydrocarbon materials being used as hydrophobic coatings with lower surface energy than polytetrafluoroethylene (PTFE) that have good mechanical performance in terms of wear resistance, friction, and hardness [43, 58]. However, the hydrophobicity of these low energy surfaces containing Si–O in the hydrocarbon coating has been reported to gradually decrease with increasing annealing temperature above 250 °C [43]. This phenomenon is presumably because of hydrogen desorption from the hydrocarbon coating, which results in significant degradation of the hydrophobic properties [59]. The thermal stability of a surface consisting of a SiO_x–DLC film and nanopillars of Si, which has been described above, has been shown to maintain its superhydrophobicity even when the substrate was annealed at temperatures as high as 350 °C [48]. The surface, however, became

superhydrophilic when the annealing temperature was further increased to 450 °C because of thermal degradation of the SiO_x-DLC film.

All the methods used to control the surface wettability of conventional materials using DLC-based materials should be applicable to the fabrication of highly functionalized superhydrophobic/superhydrophilic surfaces. However, for practical applications, further studies are needed to carefully and systematically investigate whether the surfaces combined with DLC-based materials with special wettability possess other required properties.

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Chapter 12

Smart Surfaces for Lubrication: Solid Lubricants and Adaptive Texture

T. Polcar

Abstract Modern thin films, although still being developed at laboratory scale, promise revolutionary changes in surface engineering. For automotive industry, we will focus on two classes of thin films with the potential to decrease or even eliminate oil additives, reduce friction, and improve control of tribological process.

Keywords Solid lubricant coating • Magnetron sputtering • Adaptive surface texture • Boundary lubrication

12.1 Self-Adaptive Solid Lubricant Coating

Lubrication is critical to the efficient operation of the power train. Durability and friction control is currently delivered from a complex package of lubricant additives in fully formulated oil. These additives produce, through tribochemical interaction with surfaces, nanostructured, composite, self-healing, and smart tribofilms. By far, the greatest challenge is associated with the improvement of the efficiency of compounds operating in the boundary/mixed lubrication regime. To avoid high friction and wear during asperity contact (e.g., metal to metal), low-friction tribofilms produced from additives are required. To date, the reduction of friction was and provision of adequate durability has been almost exclusively left to the modification of the lubricant and additives. This approach was very fruitful and has led to the development of very effective lubricants based on sulfur and phosphorus. Perhaps the most known is ZDDP (zinc dialkyldithiophosphates) antiwear additive, which is very effective in boundary condition [1]. To reduce friction, molybdenum dithiocarbamate (MoDTC) and also molybdenum dithiophosphate (MoDTP) have been used as additives. It is widely accepted that the friction reduction by such organic

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molybdenum compounds is mainly attributed to the formation of molybdenum disulfide (MoS_2) single sheets, as a result of complex tribochemical reactions [2].

However, there is strong legislative, operational, and commercial pressure to significantly update traditional historical lubrication. Euro 5 and Euro 6 legislations require elimination of S-, P-, and Zn-containing additives in automotive industry. With power train trends such as downsizing, low lubricant viscosity, or start–stop systems, the number of components that operates in the boundary/mixed lubrication will further increase. Finally, traditional metal surface is being replaced by application of surface treatments and/or coatings; additives developed for steel are much less effective with relatively inert surfaces, such as diamond-like carbon (DLC) coatings. The demand for surface treatments or coatings able to cope well with new environment-friendly oils, or even eliminate some of the additives, is enormous. One of the promising ways forward is the application of novel solid lubricant films, which would be able to replicate or mimic functionality of one or more additives.

12.1.1 Transition Metal Dichalcogenides: Ultimate Solid Lubricants?

As referred to above, MoS_2 , which belongs to the family of transition metal dichalcogenides (TMDs—molybdenum, tungsten, and niobium disulfides and diselenides), is a product of additive reaction, which is extremely effective to reduce friction. TMDs are, in many ways, a gift of Nature to the mechanical engineers looking for friction reduction. The hexagonal crystal structure with sixfold symmetry, two molecules per unit cell, exhibits a laminar or layer lattice structure. The attraction between the metal and dichalcogenide atoms is due to powerful covalent bonding; however, there is only weak van der Waals attraction between the lattice layers [3]. Molybdenum disulfide showed one of the lowest known frictions among solids. It is the only material where macroscopic super-lubrication (i.e., apparent loss of frictional force) has not only been simulated [4] but experimentally confirmed [5] (graphite/graphene shows super-lubrication as well, however, only in small localized contacts [6]). Another amazing feature of TMD material is violation of classical Amonton's law—their friction rapidly decreases with increasing contact pressure.

Unfortunately, pure TMDs exhibit several drawbacks when used as solid lubricants in non-vacuum conditions. They possess low corrosion/oxidation resistance, low hardness, low load-bearing capacity, and high wear. There have been a number of attempts to use them as solid lubricants or oil additives; they were prepared as thin films [3], nanotubes [7, 8], and fullerene-like particles [9, 10]. Despite all efforts, the main drawbacks of pure TMDs used as lubricants have not been overcome. High sensitivity to environmental attacks hinders both functionality and production (parts coated with TMD cannot be stored in humid air, the coating oxidizes even in dry environment).

We will focus here on TMD-based films, which are typically prepared by physical vapor deposition (PVD), most notably by magnetron sputtering. There are many

ways on how to improve properties of TMD films, such as alloying with metals (Ti [11, 12], Pb [13], Cr [14]); titanium was probably the most successful from the commercial point of view (MoST[®] by Teer Coatings Ltd., i.e., MoS₂ alloyed with Ti). Perhaps the most promising is the alloying with nonmetallic elements—carbon and nitrogen. The original idea was to combine the excellent frictional behavior of TMDs in vacuum and dry air with the tribological properties of DLC coatings. Voevodin et al. [15] prepared nanocomposite WS₂/WC/DLC coatings and W–S–C coatings with different microstructures combining WS₂ nanograins in an amorphous carbon matrix that were prepared by Nossa & Cavaleiro [16]. Again, the detrimental effect of oxidation was not overcome, and friction and particularly wear in these conditions were relatively high.

12.1.2 *Design of Solid Lubricant Coating for Lubricated Contact*

We can summarize now the requirement of solid lubricant coating based on TMD used in boundary lubrication:

- Resistance to oxidation
- Moderate to high hardness (i.e., above 5 GPa)
- Compliance with base oils and oil additives
- Ability to form thin TMD tribolayer

Coatings referred to above fulfill some of the requirements, but oxidation resistance was still an issue. To overcome reaction of the coating with surrounding atmosphere, a new concept of nanostructure design was proposed. The aim was to prepare dense coating, where the matrix could protect sensitive TMD phase. Mo–Se–C coating was the first example of such nanostructure with single randomly oriented MoSe₂ platelets embedded in an amorphous carbon matrix. The tribological results of the novel Mo–Se–C coating exceeded all expectations and clearly became state of the art: the coatings withstood a contact pressure as high as 4 GPa [17], the friction in humid air was below 0.05 [18], and the wear resistance was excellent [19]. Analysis of worn surfaces showed a very thin tribolayer (about 5 nm) formed exclusively by 002 oriented MoSe₂ phase. The coating structure below the tribolayer was modified as well; as-deposited randomly oriented and separated MoSe₂ platelets were reordered (Fig. 12.1).

However, there were two drawbacks of the new coating system, high price and hardness around 4 GPa. Main attention was then focused on tungsten disulfide alloyed with carbon. W–S–C coatings showed almost identical microstructure and tribological properties; moreover, the hardness of the coatings was as high as 10 GPa. Surprisingly, the deposition process was very robust—similar properties were obtained for DC and RF sputtering, and up-scale from laboratory to industrial device was relatively straightforward. Figure 12.2 shows final functional design of TMD–C coating. The films are deposited with Ti or Cr gradient interlayer; formation of carbides at the interface significantly increases adhesion. As-deposited film is dense

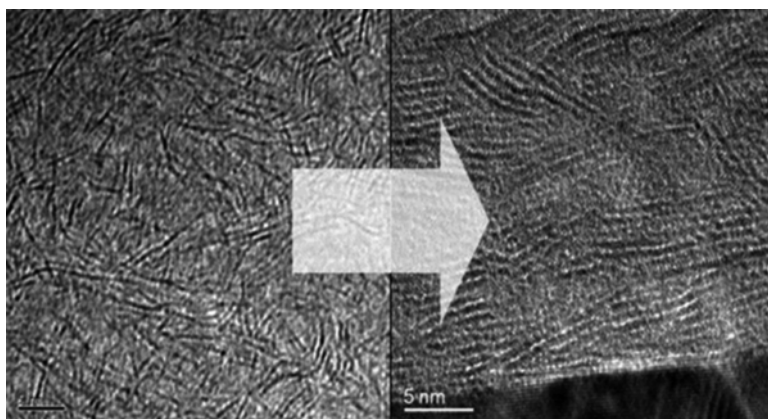


Fig. 12.1 Transformation of the Mo–Se–C film nanostructure (*left*) during sliding process (*right*). Note the change from random orientation of MoSe₂ platelets to self-ordered structure

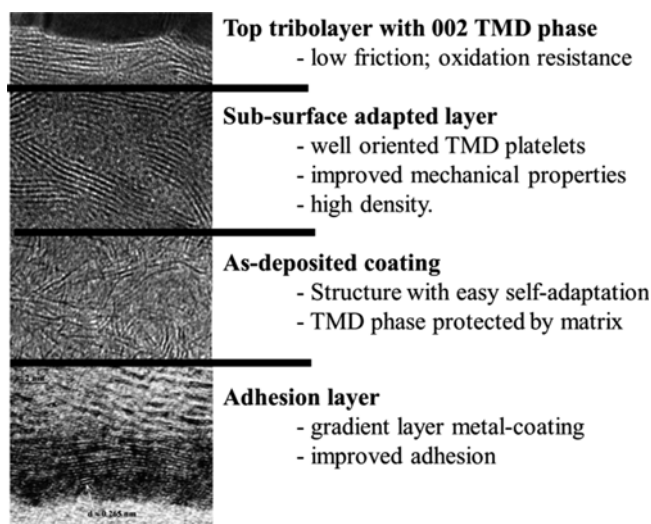


Fig. 12.2 Functional microstructural design of self-adaptive TMD-based coating during the sliding process

and featureless (i.e., columnar growth has been suppressed), and individual TMD molecular layers are dispersed in amorphous carbon matrix. Both these factors eliminate oxidation of self-lubricant phase. Sliding produces thin 002-oriented TMD tribolayer, which is oxidation resistant (there are no reactive edges) and provides low friction. Finally, subsurface structural transformation provides a material, which can immediately replenish worn tribolayer. It has been found that formation of tribolayer is accelerated by high contact pressure; in such case, the running-in process is significantly shortened. Similar concept has been studied recently by several groups

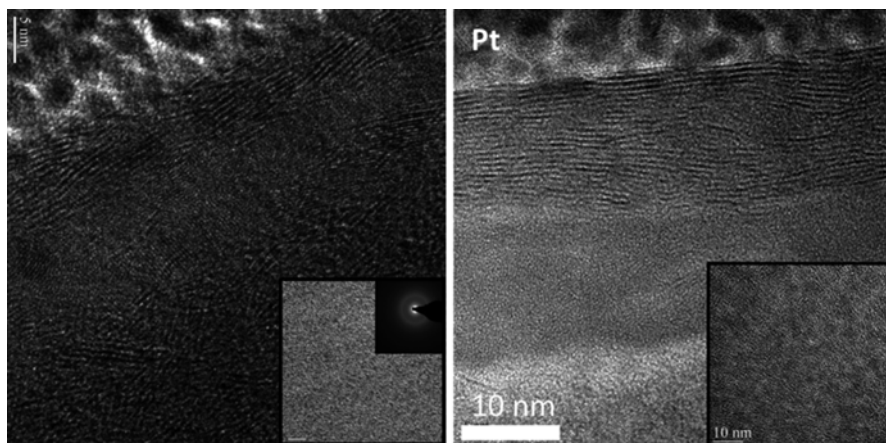


Fig. 12.3 Tribolayer produced by sliding of amorphous W-S-N coating (*left*) and amorphous W-S-C-Cr film (*right*). As-deposited structure is shown in insets

worldwide (WSeC [20] and MoSeC/Ni [21] by Fominski et al., WSC/Ti by Nyberg et al. [22], WSeC [23] by Sanchez-Lopez et al.).

It should be pointed out that formation of low-friction TMD tribolayer is a chemical process induced by sliding. Therefore, the concept could be extended to a large family of TMD-based materials. By alloying of WS_2 with carbon and chromium or by reactive deposition of WS_2 target in Ar/N_2 atmosphere, we can produce fully amorphous W-S-C/Cr [24] and W-S-N [25] coatings. It has been observed for the first time that TMD platelets could be formed from (and inside) the amorphous material (Fig. 12.3). Moreover, the coating showed remarkable ability to recover from damage; self-healing effect was observed. When part of the coating was worn out, thin WS_2 tribolayer was transferred to damaged part and adhered on the bare substrate surface [25]. Even massive damage to the coating intentionally produced by micro-machining was after some time eliminated by redistribution of solid lubricant [26].

12.2 Active Control of Surface Topography

Traditional protective thin films used in an automotive engine, such as diamond-like carbon-based coatings, are designed to exhibit optimum properties, such as hardness or chemical stability, already in as-deposited state. In other words, they are designed to retain their properties as long as possible; the changes in their properties induced by tribological processes are typically detrimental. Moreover, they are designed and optimized for constant (or limited range of) sliding conditions. However, some applications might benefit from change in surface properties or topography during the sliding application, and in such case, the use of films with “predefined” properties is limited. Gears, cams, and tappets often operate under

boundary, mixed, and elastohydrodynamic lubrication regime. It is obvious that surface treatment of such parts cannot be optimal for all wear regimes. Moreover, combination of automatic start–stop systems, dense traffic, and use of passenger cars for short distances results in dynamic change of sliding conditions.

12.2.1 Surface Texture in Sliding Contact

Surface texturing has been successfully applied to diminish friction and wear of dry and lubricated contact. Magnetic recording disk was among the first applications where laser texturing decreased static friction [27, 28]. In the case of lubricated contact, micro-cavities on the rubbing surface can act as lubricant reservoirs and enlarge local film thickness to diminish friction and wear. Moreover, dimples or grooves at the surface can eliminate the effect of wear particles by entrapping them. Such an approach has been successfully used to enhance hydrodynamic and hydrostatic lubrication of some tribological components, especially those with conformal contacts such as mechanical seals or piston rings [29]. Erdemir [30] has observed that the laser-dimpled surface provides the best performance when compared to rough and highly polished surfaces (Fig. 12.4) due to improved hydrodynamic efficiency in boundary-lubricated sliding conditions. Depending on the specific application, the depth of dimples can range from a few to several micrometers, and the diameter could be several tens of micrometers.

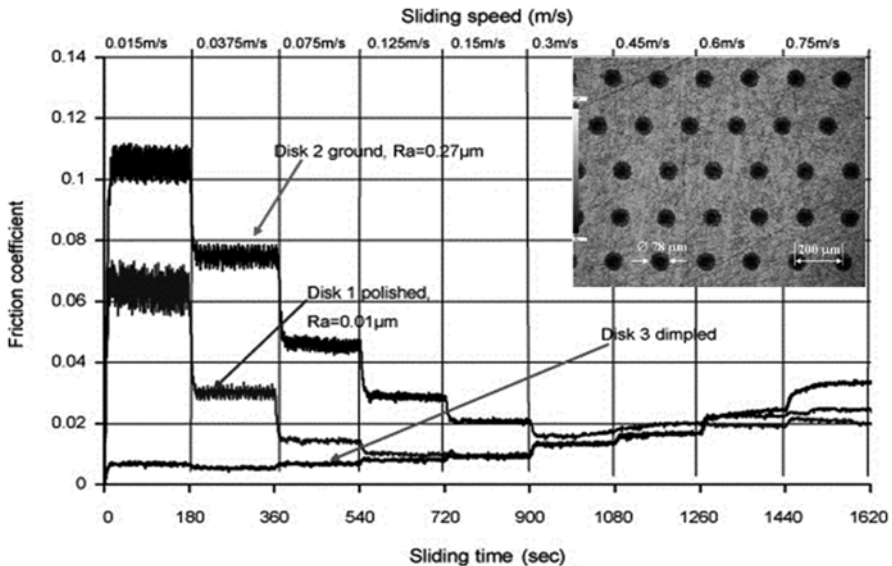


Fig. 12.4 Lubricated sliding performance of rough, highly polished, and laser-dimpled surfaces [30]

Recently, more attention is devoted to the boundary- and mixed-lubricated conformal contacts. Podgornik and Sedlacek [31] investigated the possibility of using kurtosis and skewness as the design parameters to select the optimal texturing pattern. While the surface texturing of conformal surfaces has been proven to provide beneficial tribological performance in many applications, its use within nonconformal lubricated contacts brings additional challenges. Probably the most significant is the local increase of contact pressure caused by surface irregularities within concentrated contact that can significantly reduce the rolling contact fatigue life of machine components. Moreover, the surface irregularities also influence the lubrication film thickness distribution that can even result in the lubrication film breakdown.

Zhai et al. [32] numerically simulated the behavior of micro-textured surfaces and observed that their effect on contact fatigue life depended on the lubrication regime. They also concluded that the surface cavity would not be helpful under good lubrication conditions. The pressure rippling caused by the presence of micro-features within the nonconformal contacts is one of the main differences from surface texturing applications under hydrodynamic lubrication conditions [33].

In recent years, surface texturing has been introduced to improve tribological properties also in the field of surface coatings. The effort is particularly to create hard surfaces which can be also effectively lubricated. Chouquet and Ducros [34] showed that circular micro-cavities created by a direct laser lithography-based technique can significantly reduce friction coefficient and wear rate of DLC coating. Nano- and micrometer-size pores produced by particle masking reduce friction by microlubrication effect of textured DLC [35] or TiN [36] coating surface. An effect of oil viscosity and surface nanostructure of CrN coating was studied by Gerbig et al. [37]. Oil viscosity showed a different effect on friction under different sliding velocities, which corresponds to different lubrication regimes. In dry sliding, the surface texture of thin film could improve effectiveness of solid lubricants such as MoS₂; the dimples act as solid lubricant reservoirs [38].

If we are able to control surface topography (i.e., to change texture) during the sliding process, we would significantly improve the control of sliding process and therefore reduce friction. To prepare such surface, nanoscale actuators are needed.

12.2.2 Shape Memory Alloy Thin Films

Functionalized surfaces represent a new concept in nano-tribology, where surfaces are used as direct or indirect actuators acted at controlling some of the phenomena taking place in complex tribological scenarios. Stimulus-responsive surfaces can be controlled typically through sources of heat such as electric current.

Among the potential candidate materials, Ni–Ti-based shape memory alloys are being investigated. These alloys are already used in an automotive industry as actuators (e.g., adjusting car seats). Interestingly, even in the form of sputter-deposited thin films, such alloys exhibit unusual functional properties such as shape memory effect and superelasticity. The physical phenomenon behind this unique behavior is

a reversible thermoelastic and diffusionless phase transformation between austenite (stable at high temperatures or low stress) and martensite (stable at low temperatures or high stress). Such a transformation can be both thermally or mechanically activated [39]. In particular, superelasticity is shown when the alloys are stressed in its austenitic phase, while shape memory effect is shown when martensitic alloys are heated above a certain intrinsic temperature. When the alloy is deformed in its twinned martensitic state, deformation is introduced resulting in a macroscopic shape change caused by the de-twinning process. After unloading, the deformed martensite structure remains resulting in the apparent plastic strain (pseudoplastic strain). If the alloy is now reheated above a certain intrinsic temperature, then the original austenitic phase structure and orientation are restored together with the initial shape via the thermoelastic transformation. When the alloy is cooled back down to below another characteristic temperature, the twinned martensite structure is restored without any further change in shape. This effect is known as one-way shape memory effect, as only the high temperature shape is remembered.

Nano-scratch experiments (Fig. 12.5) verified the ability of martensitic Ni–Ti thin films to recover large deformations upon heating on the nanoscale [40]. It also showed the capacity of the surface to repair itself after nano-scratches, owing to the thermally induced martensitic transformation.

If the alloy can be “trained” to remember a hot shape and cold shape, then a two-way memory can be established, where the component can be cycled between two different shapes without any external stress being applied. The training consists of introducing a specific dislocation structure and an associated stress field so as to create a microstructural and stress anisotropy within the martensitic phase. As a result, martensite variants in certain orientations are thermodynamically favored over others when cooled from the austenitic phase. The preferred nucleation and growth of these directional martensite variants enable the Ni–Ti-based alloy to remember its low temperature shape.

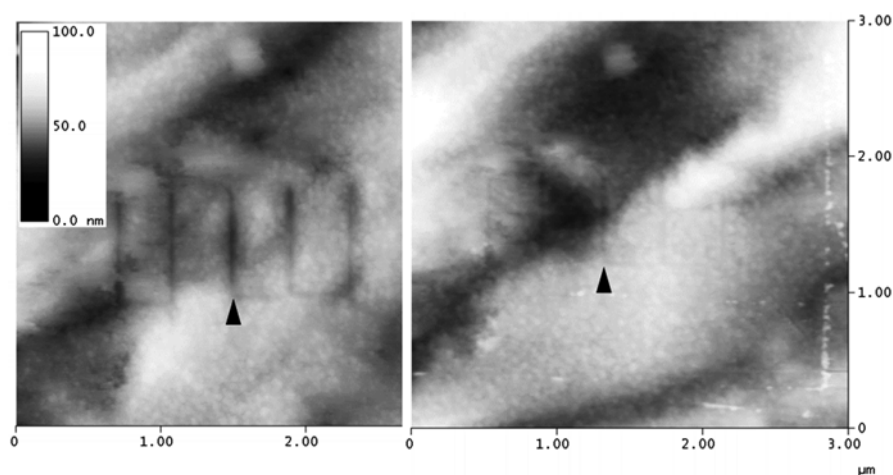


Fig. 12.5 Atomic force microscopy topographical maps of the scratched Ni–Ti surface before (a) and after (b) heating [40]

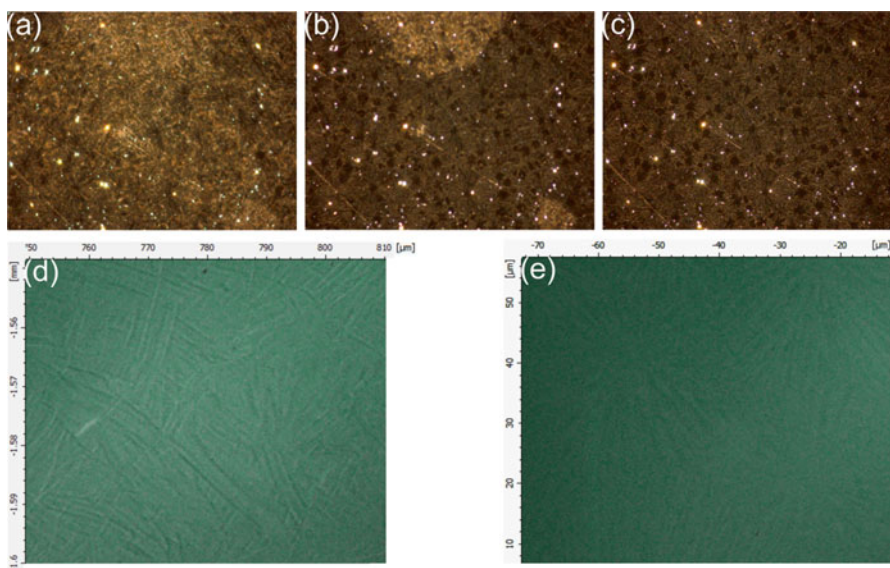


Fig. 12.6 Dark-field optical micrographs of a sputter-deposited Ni–Ti thin film at (a) 62 °C, (b) 65 °C, and (c) 71 °C. Martensitic plates nucleated on the free surface were better observed by an optical profiler (60 $\mu\text{m} \times 60 \mu\text{m}$) at (d) 50 °C and (e) 70 °C

Sputter-deposited Ni–Ti-based thin films are usually accompanied by residual compressive stresses, which can be already used as internal stress field for the two-way shape memory effect. Reversible surface features are observed on Ni–Ti thin films during thermal cycling as shown in Fig. 12.6. The dark-field optical micrographs in Fig. 12.6a–c show how the contrast changes during the reversible phase transformation, i.e., in dark field, martensitic domains are brighter than austenitic ones. Such a change is attributed to the reversible change in surface morphology as better observed in Fig. 12.6d–e. In Fig. 12.6d, martensitic plates nucleated on the film free surface are clearly observed, while upon heating these plates are replaced by chrysanthemum-like features on the surface. The out-of-plane features formed in the martensitic surfaces are on larger scale compared to the chrysanthemum-like features; thus, a change in surface roughness is produced on the nanoscale.

Zhang et al. [41] showed that temperature-controlled reversible surface indents can be made in Ni–Ti alloys as a result of indentation-induced two-way shape memory effect. Specifically, the residual stresses generated during the indentation process, in the martensitic phase, produced microstructural and stress anisotropy within the martensitic phase, enabling the film to memorize its low temperature shape. Nanoscale two-way shape memory protrusions were also successfully produced on Ni–Ti thin films by mechanical planarization of the indented surface in its martensitic state; see scheme in Fig. 12.7.

Controllable surface features in Ni–Ti-based films can be also selectively introduced by the technique of laser annealing [42]. Using this technique, shape memory properties can be spatially distributed across the surface, which can be

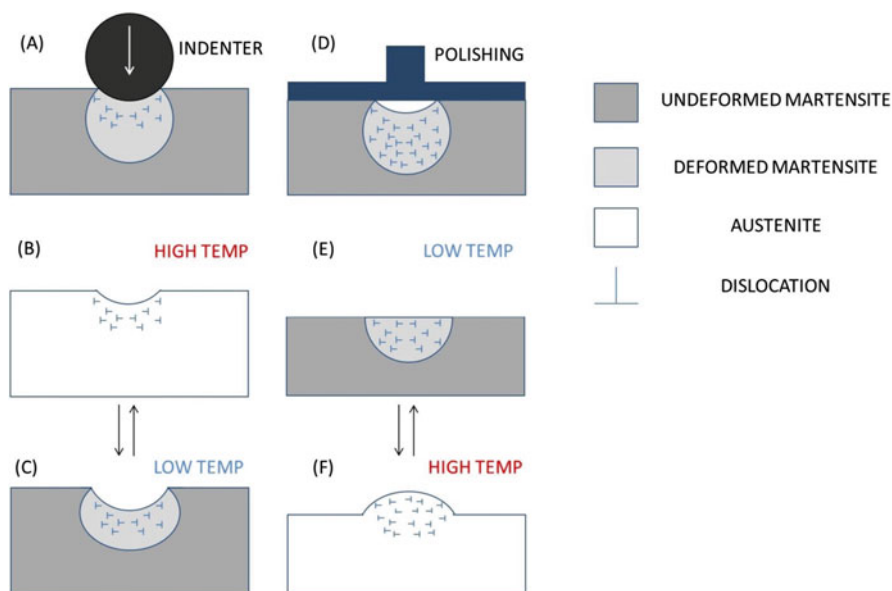


Fig. 12.7 Schematic procedure to produce shape memory protrusions on thin films

either amorphous or crystalline. In fact, a crystalline portion of the surface can be used as an actuator, while the amorphous or crystalline, but with different properties, matrix is passive and provides the restoring force.

Q. He et al. studied the surface morphology at the edge of the annealed and non-annealed (amorphous) areas at three different temperatures on a Ni–Ti thin film [43]. The roughness of the non-annealed area was almost the same at all the temperatures. In contrast, the roughness of the annealed area reduced dramatically with the increase of temperature due to the reversible phase transformation (martensite $\leftrightarrow$ austenite) from ~ 58 nm at 24.6°C to ~ 18 nm at 94.0°C .

12.2.3 Design of Nanoscale Actuators

Nanoscale actuators based on shape memory alloys described in the previous section can be controlled by temperature and/or stress. Ni–Ti alloys are relatively soft and their wear resistance is limited; however, their mechanical properties can be improved by alloying with metals (Cu, Hf, Zr). Transformation temperature depends on Ni–Ti ratio and content and type of alloying element; it can be selected from a wide range (from -20 to 200°C) covering the working temperature of majority of automotive parts. Two types of actuators are envisaged—passive and active.

Passive actuator is designed to be functional without active control. Typical example is oil temperature. At low temperature, the surface texture would be

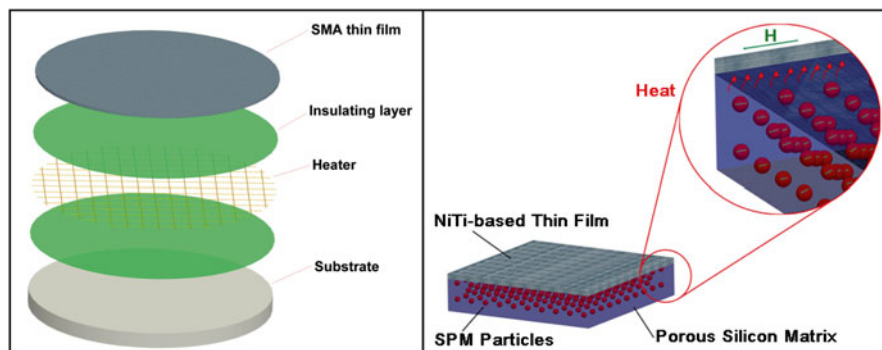


Fig. 12.8 Nanoscale heating systems for functional shape memory thin films: sublayer acting as heating plate (*left*) and heating by external magnetic field (*right*)

optimized for high oil viscosity. When temperature increases, the transformation temperature will be reached, and surface texture will change as a result of reversible crystalline transformation. Consequently, the surface texture will adapt to sliding in lower oil viscosity. The same principle could be applied to contact pressure—when certain stress level is reached, it induces transformation and changes surface topography and properties.

Active actuator requires heat input, obviously, that the transformation temperature must be designed above working temperature. Figure 12.8 shows two possible designs of such smart surface: (1) heating provided by conducting sublayer and (2) contactless heating. In the latter case, the top surface of substrate could be doped by ferro- or ferrimagnetic nanoparticles heated by external time-varying magnetic field.

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Chapter 13

Decorative PVD Coatings on Automotive Plastic

Thomas Krug and Roel Tietema

Abstract The CO₂ emission regulations have an increasing impact on the automotive industry, as these regulations are connected with severe penalties in case the average fleet emission is exceeding the limits for Europe, as imposed by the European Commission. These measures are enforcing the automotive industry to a significant increase in fuel efficiency. Basically, the emissions can be reduced, by reducing the wear losses in the powertrain and by reducing the weight of the cars, by using more and more plastic materials. Many of these parts do also have a decorative function and therefor are Chrome plated. As the plating process has to handle heavy poisoning liquids and consumes a lot of water, the industry is looking for green low cost alternatives. In this chapter the Cromatipic® process is introduced which combines a painting with a PVD coating and fulfils all requirements of the automotive industry for interior and exterior decorative parts. Finally will be introduced an integrated inline factory for performing the Cromatipic® process very cost effective.

Keywords PVD • Metallization • Inline • Decorative plastic • Automotive

13.1 Market Situation

The CO₂ emission regulations have a large impact on the automotive industry, as these regulations are connected with severe penalties in case the average fleet emission is exceeding the limits for Europe, as imposed by the European Commission. These measures are enforcing the automotive industry to a significant increase in fuel efficiency. This drives the industry into measures to reduce frictional losses by the optimization of tribological systems in passenger cars, such as further optimization of the combined friction benefits of DLC coatings with low viscosity lubricants. Another approach is weight reduction, where downsizing of engines is an example. The broader consequences of weight reduction also mean increased uses

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Fig. 13.1 Examples of vacuum metallized decorative automotive components (SIDASA Engineering S.A.)



of plastics in place of heavier metallic parts in automotive interior and exterior sections. In 2012, the global size of the automotive plastics market was around 20 billion USD by sales revenue but is expected to grow to 32 billion USD in 2018 with an average CAGR (compound annual growth rate) of 8 %. The overall global consumption is anticipated to grow from 7.1 million tons in 2012 to 11.3 million tons by 2018 at an expected CAGR of 8 % from 2013 to 2018. The majority of the plastics are targeting to replace metals consistent with the ongoing trend of weight reduction strategies for vehicles. As stated above, this is in turn strongly related to CO₂ emission reductions in passenger cars.

Reflectors and backlights of cars were among the first parts in the automotive industry which have been treated with PVD coatings. These reflectors, made from ABS (acrylonitrile butadiene styrene) or PC (polycarbonate), are coated with aluminium since the late 1980s. Initially this was done by evaporating, but, later it was primarily done by sputtering. For corrosion protection purposes, a topcoat of SiO₂ is finally applied by a plasma-assisted CVD process. As this technology is well established nowadays and used on day-to-day basis, we will exclude this routine application from this chapter.

Traditionally, automotive manufacturers include a lot of functional or nonfunctional design elements with a bright metallic chromium appearance in the interior and exterior of the cars. Examples are emblems, grills, door handles, knobs and edging elements on the dashboard (Fig. 13.1), giving the car a valuable high-tech appearance. For cost and weight reduction purposes, for many years, these parts have been made of plastic materials, mostly ABS which is electroplated with chromium first and then painted with a clear lacquer for wear and corrosion protection purposes.

However, increasing restrictions and regulations by the European Commission and governmental authorities in other parts of the world imposed strict limits or prohibited the use and handling [1] and recycling [2] of CrVI⁺ (hexavalent chromium) and other hazardous chemicals. Therefore, there is a strong push to replace the traditional electroplating technology with safer methods which by its operational principle do not use, contain or emit any hazardous materials. It has to be kept in mind that the replacement of the restricted chemicals alone will not be sufficient in many cases, as alternative means may not impart the same level of technical

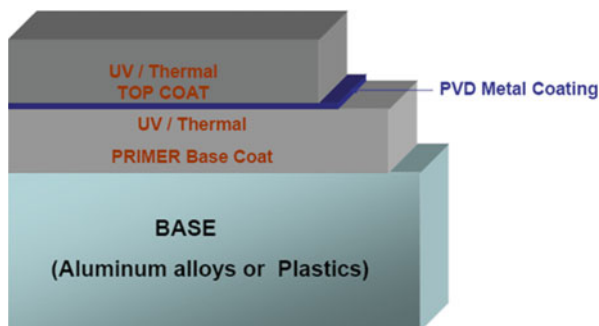


Fig. 13.2 Depiction of classic PVD coatings on plastics: base coat/metallization/top coat (SIDASA)

performance. These may also be restricted in the future or will at least involve a lot of bureaucracy to keep operating. For plastic automotive parts, which are nowadays chromium plated, the PVD technology represents such a “green” alternative.

13.2 Vacuum Metallization of Plastics

Vacuum metallizing of plastic materials and its limitations are well known and established since the 1990s [3]. For the coating of head- and backlight mirrors with aluminium, today this technology is considered as an industrial state of the art [4]. Such mirrors are coated at first with an organic base coat to promote the adhesion of the PVD layer and to achieve a brilliant surface. The aluminium layer may be evaporated or sputtered next, and finally, these layers are protected by a top coat, which may be painted or applied by plasma CVD [5]. As the mirrors are always protected by a glass or plastic cover, they are not affected by the mechanical or corrosive wear and the metallized layers will survive for the lifetime of the car.

In contrary decorative plastic parts, especially exterior parts, are submitted to strong mechanical and corrosive wear, and therefore today, the PVD technology has very limited penetration into this market.

In general, vacuum metallizing is limited by the following factors:

- Outgassing of water vapour, solvents or trapped air
- Thermal stability during coating

A good overview about the requirements and limitations of vacuum metallization of exterior automotive parts is given in [6] and [7].

The classical decorative PVD coating on plastics for automotive and other applications typically consists of three layers (Fig. 13.2): a painted or spin-coated primer base coat, which will be thermal or UV cured, the metallization and a top coat, which will be again thermal or UV cured. This base coat may have various functions like promotion of adhesion, reduction of degassing and levelling of the surface for bright shiny surface finish [7]. After metallization, another organic top coat is applied to protect the very thin (0.3–0.4 μm) chromium layer against corrosive and mechanical wear. This technology has however certain problems:

- Multilayer coatings have different thermal expansion coefficients, and therefore, they show a tendency for failure on climate change and thermal shock tests.
- The top coat on the PVD metal coating tends to blister.
- Tendency to develop surface defects like pitting, orange peel, roughness and non-uniform thickness especially on 3D parts.

Although during production of these PVD coatings no use or generation of Cr VI^+ happens and no hazardous materials are produced or emitted, above-mentioned disadvantages are limiting the use of this technology for most automotive applications.

13.3 The Cromatipic® Process

The Cromatipic® process has been developed by SIDASA [8] and applied for patent protection [9].

In contrary to the classical three layer process, the Cromatipic® process consists of just two steps, the base coat and a sputtered metallic finish as shown in Fig. 13.3 [10].

A cross section of such coating is shown in Fig. 13.4. The thickness of the base coat is typical 20–40 μm . As the base coat does not contain any organic solvent and is cured by UV light, no solvents are emitted during curing step, i.e. the Cromatipic® process does produce very little waste and has therefore no environmental impact.

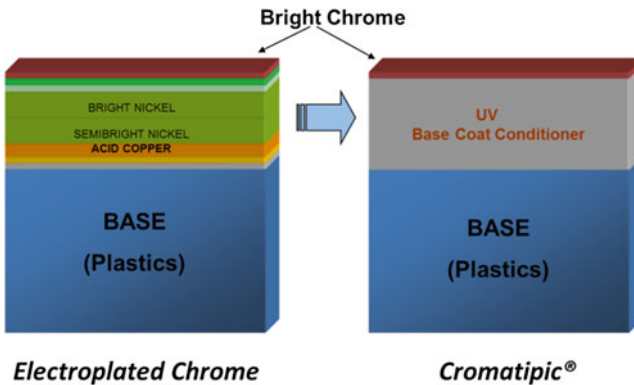


Fig. 13.3 Cromatipic® layer structure compared to an electroplated hard chrome coat (SIDASA)

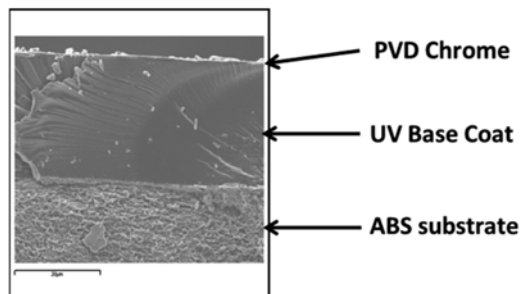


Fig. 13.4 Cross section of a Cromatipic® layer structure (SIDASA)

Table 13.1 Production steps of wet plating compared to the Cromatipic® process

Plating on plastics		Cromatipic®
• Cleaner	• Accelerator	• Pre-treatment
• Rinse	• Rinse	
• Conditioner	• Nickel flash	• Radcure UV
• Rinse	• Rinse	
• Neutralizer	• Acid copper	• PVD coating (arc/sputtering)
• Rinse	• Rinse	
• Hydrochloric Acid	• Nickel's x3	
	Semi-bright	
	Bright	
	Micro	
	Discontinuous	
• Rinse	• Rinse	4 Basic stages
• Catalyser	• Chromium	
• Rinse		
13 Basic stages		

This makes the process more practical and requires only four steps (cleaning/painting/ UV curing/ metallizing). Overall, it is much simpler and easy for an inline integrated production process. In contrary, an electroplated chromium coating consists of at least five metallic layers, requiring handling with various poisoning liquids and consumption of a lot of water for intermediate and final cleaning steps (Table 13.1). Also, the hard chrome plating process is mainly limited to acrylonitrile butadiene styrene (ABS) and ABS-polycarbonate (ABS-PC) materials, while the Cromatipic® process can be applied to a wide choice of materials like ABS, ABS-PC, acrylonitrile styrene acrylate (ASA), PC, polystyrene (PS), polyethylene terephthalate (PET), polypropylene (PP), polyphenylene (PPE), polyamide (PA), polyamide-melamine formaldehyde (PA-MF) and polyphthalamide glass filled (PPA-GF), PA-GF [10], which gives the designer much more flexibility for technical and cost optimizations.

To be used in the automotive industry, the coated parts have to perform well and pass various technical tests for wear, corrosion and thermal resistance. In the Appendix is listed a detailed summary of the qualification tests that parts, processed with the Cromatipic process have passed successfully. Today a variety of parts for automotive and non-automotive applications are in mass production.

13.4 Vacuum Metallizing

13.4.1 Batch Coating Systems

Today, the majority of all metallized parts used in the automotive industry are processed in batch coating systems. Initially, the systems had the design of horizontal tubes; today mostly vertical chambers with two doors are built by various manufacturers (Fig. 13.5) like Kolzer [11], VTI® [12], Leybold Optics [13] and others.



Fig. 13.5 Two-door batch vacuum metallizer (KOLZER)

Although some of these machines are built for thermal evaporation of aluminium, there is no principal limitation to build these machines with magnetron sputtering sources with chromium targets to achieve the much desired chrome colour.

Each door is equipped with a full set of substrate fixtures. When the first door is closed to perform the coating cycle, in the second (open) door, the spindles with coated parts can be replaced and maintenance like vacuum cleaning can be performed. After the first cycle is finished, within a few seconds, the first door is opened and the second door is closed, to start the second cycle. This concept makes these systems highly productive; however, the capacity for chrome coating is limited to approx. 10–30 m²/h, depending on the chamber size and specific coating cycle.

Main advantage of the batch coating systems is that their capacity can be ideally matched to the required production volume, and the related investment can thus be used in a more efficient manner. With growing capacity needs, the existing system can be multiplied as required. If multiple systems are installed, there is the security and flexibility that production can be continued (at lower capacity) if one of the systems fails or is down for general maintenance.

Main disadvantage is the fact that there is no continuous production flow and the loading/unloading in practice is not automated, i.e. there is a lot of manual operation required, with the related high personnel costs.

13.4.2 The Inline Metallizer: Metalliner®

13.4.2.1 General Considerations

Although the inline PVD coating technology is well established since the 1970s, e.g. for the coating of architectural glass, there are some quite significant differences to be considered in the design of an inline coater for plastic parts.

While glass is a flat substrate with always the same dimensions (typically 3×6 m), automotive parts will always be more or less 3 dimensional. This has an

important impact on the design of the machine, not only for the ports to enter or leave the vacuum chamber but specifically for the gas and pressure separation of different process chambers.

Plastic materials are quite different in their thermal stability and their outgassing behaviour. Some of these materials do not only desorb water vapour from the surface but will also be outgassing remaining solvents and/or water vapour from the bulk material. ABS materials are most commonly used in the automotive industry because of its mechanical and thermal stability, controllable moderate outgassing behaviour and the easy paintability. It is the only plastic material which can be directly metalized without special pre-treatment with good adhesion of the PVD coating. However, there is a trend for more flexibility in the choice of the material, not only to save weight and costs but also to engineer soft front parts of the car for protection of pedestrians in case of an accident. Beside this, not all components require the mechanical strength of ABS, which is especially the case for pure decorative design elements without any mechanical function like strips around the dashboard.

If plastic materials have to be coated, it is vital to start the coating process at a sufficient low base pressure, which should be in the lower 10^{-2} Pa range or better. Otherwise, the desorbing gases from the coating side or back side of the part will react with the metal vapour during the coating process, resulting in discoloration and poor adhesion.

In a batch coating system, the different outgassing behaviour of the different plastic materials can be easily compensated, just by extending the pumping time to reach the necessary starting pressure, while the inline system has to work with a specific fixed cycle time, especially when it is integrated in a full size automated factory.

Therefore, the Cromatipic® process is ideal to be combined with an inline PVD coating system.

As the paint does not contain any solvent, there is no outgassing from the paint and the desorption of water vapour from the surface is independent from the base material.

Finally, special care has to be taken for the accumulation of dirt in the vacuum chambers, as the coating material will coat not only the parts but also frames/substrate holders and the vacuum chamber itself. While in a batch coating system such parts can be easily cleaned between the batches, the inline system should not be opened during the lifetime of the consumable materials, in this case the targets of the magnetrons (144 h).

13.4.2.2 Basic Lay Out

The Metalliner® is a vertical modular coating system, build from ten identically dimensioned segments, which are equipped with the different process modules (pumping, transportation, sputtering, PECVD). The vertical orientation has been chosen to avoid dust, falling from chamber walls or coating sources onto the parts, as this would result in defects in the coating. The different modules are built on rails and fixed to each other (Figs. 13.6 and 13.7).

This design allows building this machine in different length and with different process modules (Fig. 13.8), shorter for a semi-inline system for lower as well as longer for higher capacity. The system can also be equipped with reactive modules to get certain colours like gold, grey or black and others by coating of TiN, ZrN,

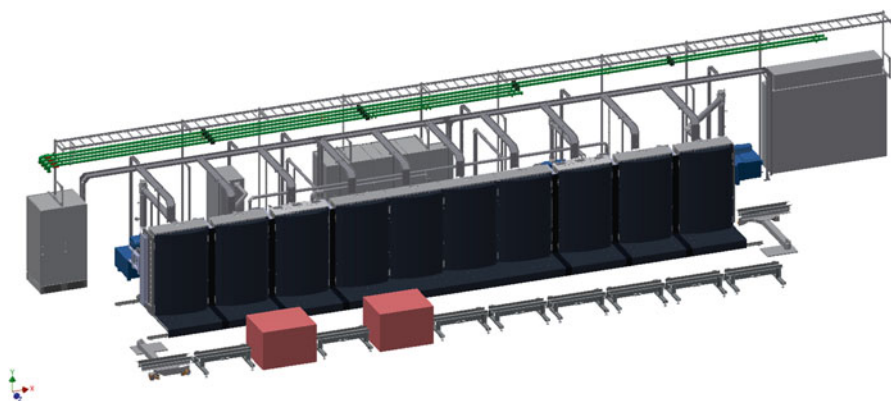


Fig. 13.6 Basic layout of the Metalliner®



Fig. 13.7 The Metalliner® during assembly

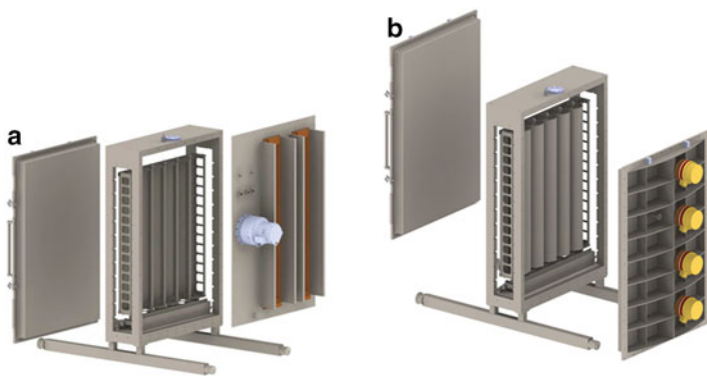


Fig. 13.8 Process module for double magnetron sputtering (DMS) (a) and for circular arc technology (CARC) (b)



Fig. 13.9 Big automotive grill coated in the Metalliner®

DLC, etc. As the chambers are not fixed to the floor but build on rails, it is quite easy to change the initial process modules or add additional process modules. Also, the system is equipped with a rack return system to allow a continuous operation and automatic loading and unloading of substrates.

The different carriers are designed for a loading volume of $1,200 \times 1,500 \times 200$ mm ($l \times h \times w$) which therefore permits also big parts to be coated (Fig. 13.9).

The machine can be operated with a tact time of 60 s for 2D parts, i.e. a capacity of $108 \text{ m}^2/\text{h}$ (projected surface) and 180 s in case the parts are rotating during the coating process, which results in a capacity of $94 \text{ m}^2/\text{h}$ (projected surface). The thickness of the chromium layer is typically $0.4 \text{ }\mu\text{m}$ and the lifetime of the targets is 6 days in an uninterrupted three-shift operation.

The schematic lay out of the system is given in Fig. 13.10. The parts are entering the machine through typical load lock and crossover chambers, supported by a cryopanel, which are all separated by high vacuum valves. This ensures that the outgassing of the parts, as earlier discussed, can be kept under control and no discoloration will happen. This is especially the case when other plastic materials than ABS are used with the Cromatipic® process. In the next chamber, the surface of the plastic parts is activated by an argon glow discharge, to provide a good adhesion of the chromium coating. From chamber 4 to chamber 7, the carriers are continuously moving, where the coating is applied in chambers 5 and 6 by magnetron sputtering. Again separated by high vacuum valves, an optional SiO_2 topcoat can be applied for parts with severe wear conditions by a PECVD process, using precursors like TMS or HMDSO. Finally, the carriers are discharged from the Metalliner® in two chambers similar as in the entry. Subsequently the carriers will be unloaded and automatically returned to the loading station.

13.4.2.3 Transport System

Innovative designs for the transportation and the carrier system are included in the design of the Metalliner®.

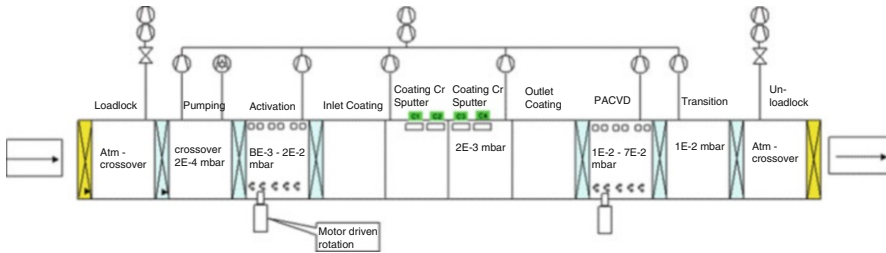
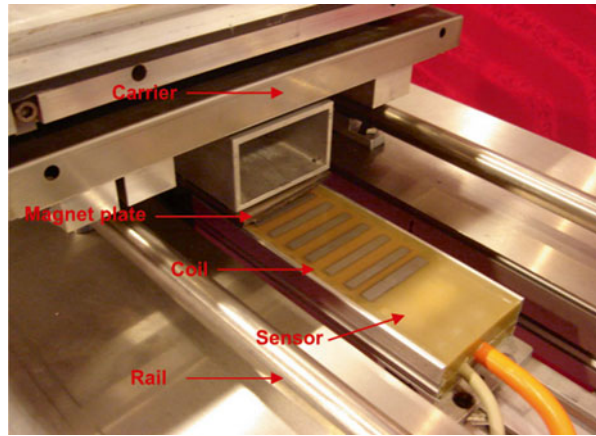


Fig. 13.10 Schematic layout of the Metalliner®

Fig. 13.11 Linear Motion System (LMS)



One of the most critical parts for the design of an inline system are the rotary feedthroughs which are driving the substrate (like in case of glass coatings) or the substrate carriers. Such a drive system is required at least in each vacuum section of the machine, and a rotary feedthrough is always a potential vacuum leak. To avoid such risk, the Metalliner is equipped with an inductive magnetic drive system, the Linear Motion System (LMS) [14] as shown in Fig. 13.11.

Each magnetic coil of that system can be individually actuated and allows an exact control of the motion for each of the individual carriers. With the Hall sensors as position detectors, the positioning of the carrier in the individual vacuum chambers and on the carrier return system is controlled. The magnetic field forces generated by the coils of this linear motor system permit the contactless energy transfer for steering the movement of the individual carriers. At the vacuum sections, the system is assembled below the chambers, i.e. no feedthrough for cables is required. Besides the rollers of the carriers, there is in the vacuum chambers no mechanical moving part which could fail. The system power is also strong enough to actuate a rotation of the substrates required for 3D parts during the coating step (see below).

Fig. 13.12 Rack with backside shields, loaded with dashboard frames before metallization



13.4.2.4 Loading of the Metalliner®

One fundamental challenge in any inline system is the accumulation of undesired coatings in the vacuum chamber, which will flake off at a certain time when these dirty coatings are getting too thick. If these flakes are falling on the parts to be coated, these parts will have optical defects, and therefore, they are waste as they cannot be reworked. To reduce these effects, the racks mounted on the carrier are provided with shields (Fig. 13.12). These shields are collecting these vapour streams, in that way additionally reducing the undesired coating contaminating the chamber walls. Therefore, an uninterrupted operation of the Metalliner® is achievable until the target life time of appr. 144 h is reached.

The racks leaving the vacuum chamber with coated substrates can be easily cleaned when the coating is getting too thick and begins to flake off. The parts to be coated are mounted on frames, which may be manually or automatically loaded on the racks.

13.5 Factory Integration

The Metalliner® may be operated as a standalone unit; however, the most cost-effective way is the integration into an automated factory, where the painting process is done immediately before the metallization. Transfer of the lacquered objects

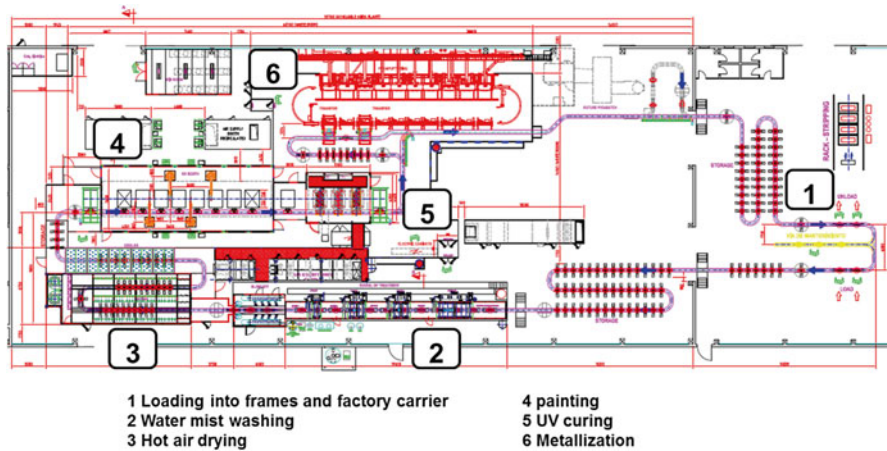


Fig. 13.13 Integrated factory for painting and metallization

will be done without the objects being touched by operators. Figure 13.13 shows the schematic layout of the factory, where the Metalliner® is integrated.

The objects are manually placed into vertical frames (Fig. 13.13, pos. [1]) and then loaded by an automated system in the factory transportation system, which circulates the frames on rails through the entire factory, finally arriving metallized at the same place.

Since the parts may be affected by dust particles, they are washed by water mist [2] and dried with hot air [3].

For painting, the frames are turned into a horizontal position, to achieve a uniform thickness of the paint. The painting will then be applied by a robotic system [4] as shown in Fig. 13.14.

The robots will follow the basic contour of the objects, to achieve a uniform distribution, but save paint at the location, where the object is open (compare Fig. 13.14) or no object is placed. Therefore, always the frames have to be loaded with the same parts at the same position; however, the load may differ from frame to frame. Each frame is numbered, so the robots can identify the loaded parts and execute the appropriate program.

After painting, the paint will be cured by UV light from both sides top and bottom, to achieve a uniform curing, even with complex shaped parts or for 3D parts which will rotate during painting and curing [5].

After turning the frames again into a vertical position, they will be loaded by an automatic handling system into the rack of the Metalliner® and will be moving with the carrier of the Metalliner® through the coating process [6]. Due to the identification of each frame, the metallization process may be adjusted from frame to frame if required. The rack return system will move the carrier to the unloading position, where the frames are taken out and placed again into the carrier of the factory transportation system. This system will deliver the parts then back to the unloading area of the factory [1].

As the frames are also getting painted, this paint has to be removed, before they are loaded again into the Metalliner® to avoid arcing and coating defects.

Fig. 13.14 Robot painting on horizontal frames



13.6 Summary

It has been shown that the Cromatipic® process, which received all technical approvals from the automotive industry, is a clear green alternative for the classical wet chemical coating process, without handling or containing any hazardous materials. With the development and integration of the Metalliner® into an inline factory, a series mass production of PVD-coated plastic has been realized. Due to the automated integration with no manual operation steps, there is also a cost advantage against the chemical plating process. This is a real breakthrough for the use of the PVD technology for decorative parts for interior and exterior decorative elements of cars with an attractive chrome finish.

Appendix: Overview of Tests Performed on Cromatipic® Processed Parts

Summary of the various tests performed on Cromatipic® processed parts ([1.3.3])

Test	Method/standard	Description	Requirements	Results
<i>Adhesion</i>				
Cross-hatch test	EN ISO 2409 ASTM D3359-97 TL-528 GMW14668		GT 0–GT 1	PASS
Saw grind 22 tooth/inch 16–18 tooth/inch	ASTM B 571 TL-528 WSS—MIP83 GMW 14668		No lifting or peeling	PASS No lifting or peeling

(continued)

(continued)

Test	Method/standard	Description	Requirements	Results
<i>Abrasion</i>				
Crockmeter	TL-226-3.12.3.2 (PV3906)	100 Crockmeter strokes against dry cloth	Evaluation of surface: no visible change compared to as received condition	PASS
Rub abrasive test	QDS ME 128 (Sidas internal method)	Double rubs with abrasive cloth		>100 RTv
Taber abrasion	GM 9515 P	Wheel-type CS 10 Load:500 gr Number of cycles required to wear the coating through to the substrate	Non-specified acceptable criteria	126 cycles
Thumbnail hardness	GM 9507P	Test samples showing marring by scraping shall not be acceptable	No marring	PASS
<i>Chip resistance</i>				
Gravelometer	GM 9508 P	Conditioning 4 h at -30 °C Test temperature: -30 °C Angle: 90° Spray pressure: 70 psi Road gravel 9, 5/16 mm	Chipping rating should be greater than 3	Chip rating = 9; PASS
Gravelometer	ASTM D3170-07	Test temperature: -18 °C	No C or D chip sizes allowed	Result = 5B, PASS
<i>Corrosion</i>				
Cass test	ASTM B368-97 GM 4372M-92	Cupro acetic salt spray test 22 h	The coating shall be free of corrosion on all significant surfaces when examined at normal reading distance (no corrosion, blisters or flaking found)	PASS
Cass test	ASTM B 368 UNE EN ISO 9227:07 GMW 14668 WSB-M1P83 TL-528-4.1	Cupro acetic salt spray test at 50 °C—24–48 h	No change in appearance, no visually discernible corrosion when assessed from a distance of 60 cm under optimal lighting	PASS Up to 144 h without any change
Climate test	96 h PV 1200 +24 h CASS VW TL 528	1 h up 80 °C 80 % h 4 h to 80 °C 80 % h 2 h down -40 °C 30 % h 4 h to -40 °C 30 % h 1 h to 23 °C 8× cycles +24 h CASS	No change in appearance	PASS

(continued)

(continued)

Test	Method/standard	Description	Requirements	Results
Environmental cycle test	TL-528—3.3.1. PV 1200	1 h up 80 °C 80 % h 4 h at 80 °C 80 % h 5 h down -40 °C 30 % h 4 h at -40 °C 30 % h 1 h at 23 °C 8× cycles	No change in appearance (no blistering, no cracking, no colour change, etc.)	PASS
Environmental cycle test	TL 528P PV 1210 1°-neutral salt spray test (DIN 50021)+2°-Standard aging (DIN 50014)+3°-Humidity test	4 h at NSS (DIN 50021) 4 h at aging climate (DIN 50014) 16 h at 40 °C 100 % humidity = 1 cycle×60 cycles	For exterior parts 60 cycles are required No change nor damage in the coating	PASS
“Russian” mud test	NES. Decorative chromium plating 4.5.2. (method A)	Ca chloride mud + 60 % Humidity@23 °C	After 336 h: electroplating part fails and Cromatipic part PASS	PASS
Salt spray test	ASTM B-117	144/24 h	No change in appearance	PASS >480 h
Environmental cycle test	TL-528-3.3.2 PV 2005	Holding time: 60 min at 23 °C, 30 % h Cooling-off phase: 150 min from 23 °C to -35 °C, 30 % h Holding time: 120 min at -35 °C, 30 % h Heating up phase: 150 min to 45 °C; 30 % h Moisting phase: 180 min; 45 °C, 95 % h Holding time: 240 min, 45 °C, 95 % h Drying phase: to +42 °C 30 % h Holding time: 450 min at 42 °C, 30 % h Cooling-off phase: 60 min, 23 °C, 30 % h 50× cycles	No change in appearance (e.g. cracks, pores, marks)	PASS
<i>Water resistance</i>				
Humidity test	TL 226-3.11.1 Condensated water constant climate DIN EN ISO 6270-2 DIN EN ISO 4628-2	240 h at 40 °C	No change in appearance, no blistering	PASS
Hot water resistance		240 h at 40 °C	Without any change	PASS
<i>Temperature resistance</i>				
Temperature resistance	TL 528-3.1	6 h at 110 °C	No change in appearance, crosscut test with no stripping of coating	PASS

(continued)

(continued)

Temperature resistance	TL 528-3.2	500 h at 90 °C	No change in appearance, crosscut test with no stripping of coating	PASS
<i>Aging resistance</i>				
Hydrolysis aging	TL 226-3.12.1	72 h 90 °C >96 % h	No changes in colour or haptic characteristics should pass adhesion and Scratch resistance	PASS
QUV-B 1000 h		cycle: 4 h UVB lamp 4 h condensation 50 °C	No change in appearance	PASS
QUV-2000 h		Cycle: 4 h UVB lamp 4 h condensation 50 °C	No change in appearance	PASS

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