

2. Literature review.

In this chapter, literature related to tribological properties of various type of coatings have been discussed. Special attention to the tribological aspects of the multilayer hard coatings, nanocomposite, and soft coatings are discussed. The development of hard ceramic coatings is explained in detail and mechanisms related to various tribological behaviours have been discussed at room and high temperatures.

2.1. Introduction.

Friction and wear have always been the major concerns for significant energy loss and failure of machine parts in industries. Over the years researchers have tried to reduce the energy dissipation in machine parts and enhanced their durability through advanced lubrication technology. The machine components are exposed to harsh and harmful environment (such as high load, high vacuum, and extremely high and low temperatures). Most of the oil based lubricant and greases reduce friction between the sliding pairs by shearing of oil molecules across the solid – liquid – solid interface [28], and are volatile at high temperatures, which leads to failure of the lubricated component and potentially other unrelated components when the vapor from the lubricant condenses or reacts with the surfaces. Therefore, the need for an efficient and reliable machine requires the need of highly resistant materials. The cost of producing new highly resistant materials, as well as the production of machines from these materials, can be very high [29]. Hence the use of protective coatings allows for improving the reliability and maintaining manufacturing cost at reasonable level. On a broad level, two types of protective coatings are generally applied for improving the tribological performance of machine parts in industries. First being the hard ceramic coatings like TiN, CrN, CrCN, TiCN, TiO₂, DLC, etc., deposited through CVD, PVD or thermal spraying [30–40]. Second being the

soft polymer coatings like polyurethane, epoxy resin, phenolic resin, polyamide, etc, deposited through spraying, spin coating or dip coating. These coatings are often enforced with nano and micro-sized fillers to enhance their tribological properties [41–49]. The hard ceramic coatings and the soft polymer coatings, both possess their own advantages and disadvantages, which are explained later in the chapter. The hard coatings under study were developed from PVD technique. Therefore, before diving into the tribological aspects of hard and soft coatings, it is necessary to know how the coatings are deposited through PVD and what are the advancements made in the field of PVD technique.

2.2. Physical vapour deposition (PVD)

Physical vapour deposition (PVD) is an innovative technique to fabricate coatings. It is an environment friendly process, making it popular even further. It is broadly classified into three types: evaporation, molecular beam epitaxy, and sputtering. While evaporation is limited to materials with low melting points, the refractory materials cannot be used. Molecular beam epitaxy is mainly used for coatings in research purposes. **Figure 2.1** shows the schematic diagram of a PVD system.

Sputtering is a PVD process used for industrial applications. Sputtering involves the ejection of individual atoms from the surface of a target through ion bombardment and then its deposition onto the substrate. All glow discharge processes involve sputtering since it is impossible to sustain a glow discharge without an electrode. Although the deposition process is slower and the yield is low, sputtering is a good technique for coating as it allows for controlling the layer thickness and provides a coating with a smoother finish. Based on modes of operation the sputtering is further classified into different types, 1) diode, and 2) magnetron sputtering.

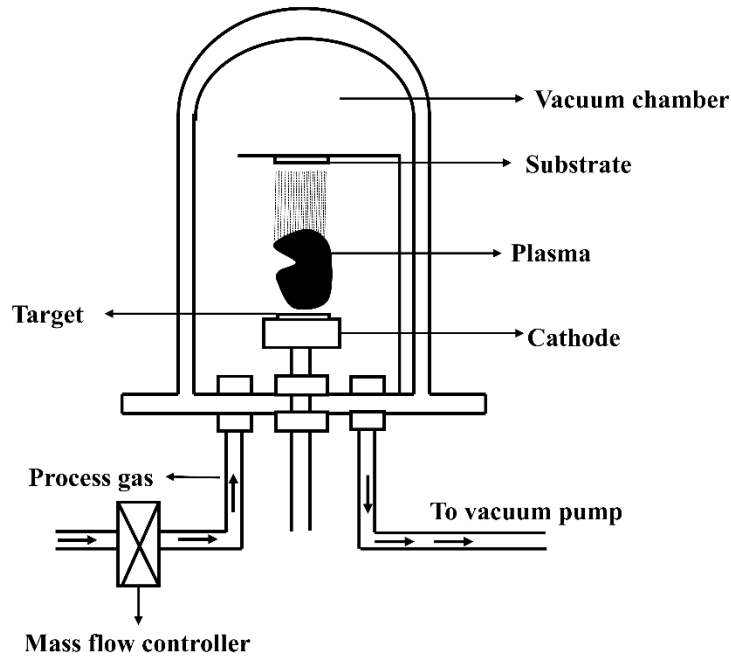


Figure 2.1. Schematic representation of PVD technique.

2.3. Diode sputtering.

In this, the plasma's free electrons are quickly evacuated from the negative potential electrode (cathode). The electrons in the shells of these atoms separate as these accelerating electrons clash with neutral gas atoms (Argon) in their route. As a result, the gas atoms turn into positive ions and speed towards the cathode, generating sputtering. Some free electrons in plasma find their way back to the final electron layer of gas ions, restoring the ground state of the gas atoms. The release of energy in the form of photons occurs when an atom returns from a high energy level to its ground state, and these photons are what cause the plasma to glow. One of the major problems with diode sputtering is the low coating rate, which causes the target to heat up and damage its atomic structure.

2.4. Magnetron sputtering.

This type of sputtering incorporates the use of strong permanent magnets and electric current to produce magnetic fields transverse to electric fields to generate plasma. The basic modifications of sputtering include:

- Trapping of secondary electrons in cycloidal trajectories near the target to reduce excessive bombardment. This does not overheat the substrate. Thus, temperature sensitive materials can also be used.
- Higher deposition in comparison to conventional techniques. Thus, it can be used for economical, large scale industrial applications.

Figure 2.2 shows the schematic representation of magnetron sputtering. Magnets are positioned in such a way that one of the poles is positioned at the central axis of the target, while the second pole is formed by a ring of magnets around the outer edge of the target. The ionized argon ions bombard on the target attached at cathode. The bombarding argon ions knock out atoms from the target element. The liberated target atoms travel through the vacuum environment to deposit onto the substrate. The secondary electrons are also emitted from the target during the bombardment. For most sputtering systems, the kinetic energy of the incident ions is in a knock-down regime [50]. In this regime, the kinetic energy of the ions is high enough to cause secondary collisions. During this energy transfer, the ions often excite electrons from the target. The emitted electrons are termed as secondary electrons, which are accelerated towards the anode and participate in plasma generation by ionizing sputtering gas. Different magnetron geometries include cylindrical, conical and planar geometries. This can also be used in combination with reactive mode to produce compound coatings. The reactive mode of magnetron sputtering uses of gasses like nitrogen, methane, acetylene, etc., along with

the argon gas to deposit nitrides and carbides, respectively. The micro structure can also be controlled during coating growth in magnetron sputtering.

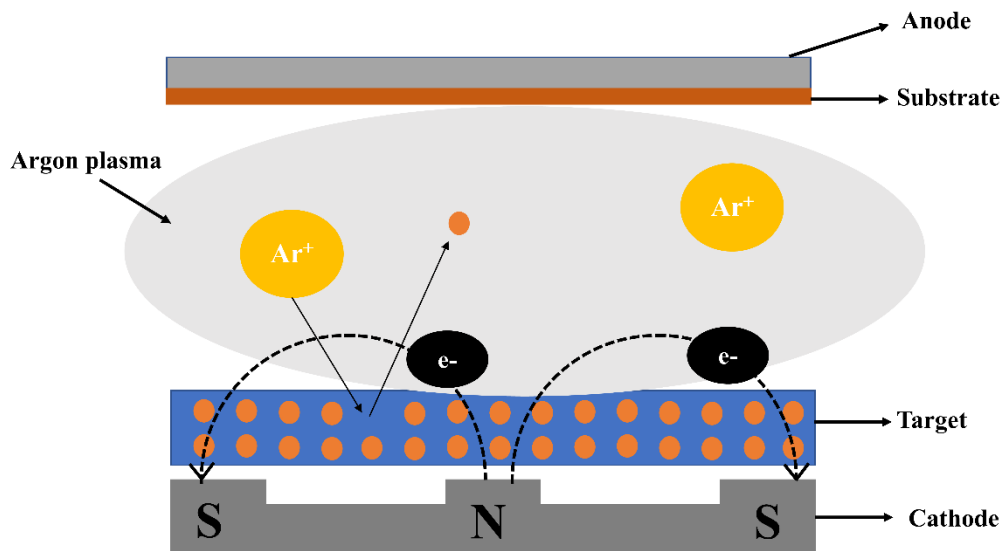


Figure 2.2. Schematic diagram of magnetron sputtering.

2.4.1. Types of magnetron sputtering on the basis of design of cathode.

Based on the design of cathode in magnetron sputtering, the magnetron sputtering systems are characterized into two types: 1) Balanced magnetron sputtering, and 2) Unbalanced magnetron sputtering. There are minor design changes in sputtering systems containing balanced and unbalanced magnetrons. However, there is a significant difference in the performance between the two types of magnetrons. The plasma is strongly confined to the target region in a balanced magnetron sputtering system. A dense plasma zone usually extends 60-80 mm from the target surface. Films formed on the substrates in this region will be bombarded with ions at the same time, which can have a significant impact on the structure and properties of the growing film. Substrates are positioned outside of this region. On the other hand, will be in a zone of low

plasma density. As a result, the ion current drawn to the substrate (usually, $1\text{mA}/\text{cm}^2$) is insufficient to alter the structure of the film. Applying a negative bias to the substrate increases the energy of bombarding ions, but leads to an increase in residual stress and defects in the film. Hence, depositing fully dense films on large, or complex components through balanced magnetron sputtering.

A strong flux (greater than $2\text{mA}/\text{cm}^2$) of relatively low energy (100eV) ions is often selected to deposit dense films without creating significant intrinsic stresses [51]. The unbalanced magnetrons can easily provide these conditions. The outer ring of magnets in an unbalanced magnetron is stronger than the core pole. Not all field lines between the central and outer poles of the magnetron are closed in this scenario, but some are directed towards the substrate, and some secondary electrons can follow these field lines. As a result, the plasma is no longer tightly bound to the target region and is free to flow towards the substrate. Hence, strong ion currents can be recovered from plasma without the need to bias the substrate externally. Strong substrate ion flux densities of more than $5\text{mA}/\text{cm}^2$ have been reported by earlier researchers with the use of unbalanced magnetron sputtering [50,52]. **Figure 2.3** shows a comparison between plasma confinement of balanced and unbalanced magnetron sputtering. Thus, an unbalanced magnetron serves as a highly efficient ion source in addition to producing a high flux of coating atoms (as compared to balanced magnetron). Furthermore, the target current is proportional to the ion current drawn at the substrate. The rate of deposition is likewise proportional to the desired current.

Despite the advantages of unbalanced magnetrons, uniformly coating complicated components at reasonable rates from a single source still remained a challenge. As a result, multiple magnetron systems have been introduced to commercialise this technology. The magnetic arrays of nearby magnetrons in a multiple magnetron system can be designed with either identical or opposite magnetic polarity. In the first situation, the configuration is characterised

as “mirrored”, whereas in the second case, it is described as a “closed field”, as illustrated in **Figure 2.4**. The field lines in the mirrored casing are directed towards the chamber walls. Following these lines, secondary electrons are lost, resulting in a low plasma density in the substrate region. In contrast, the field lines are linked between magnetrons in the closed field configuration. The substrate is in high density plasma area, therefore there are few losses to the chamber walls. Kelly et. al. reported that operating in closed field mode results in an ion- to-ion atom ratio incident at the substrate 2-3 times greater than the mirrored, or single unbalanced magnetron configurations under the same conditions [53].

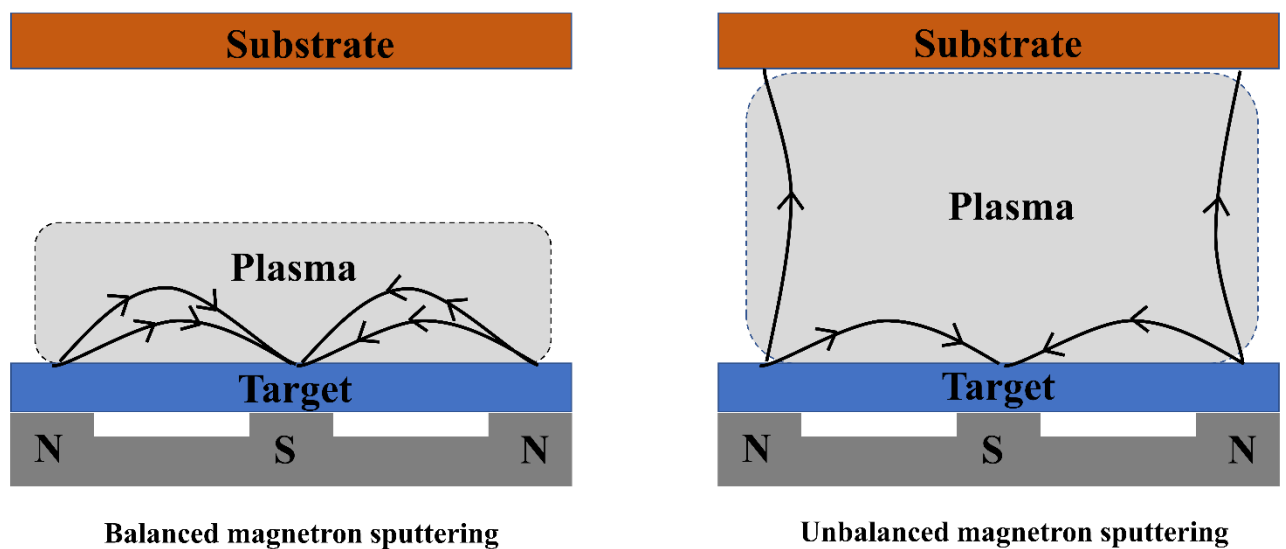


Figure 2.3. Schematic diagram representing the formation of plasma in a balanced and unbalanced magnetron sputtering systems.

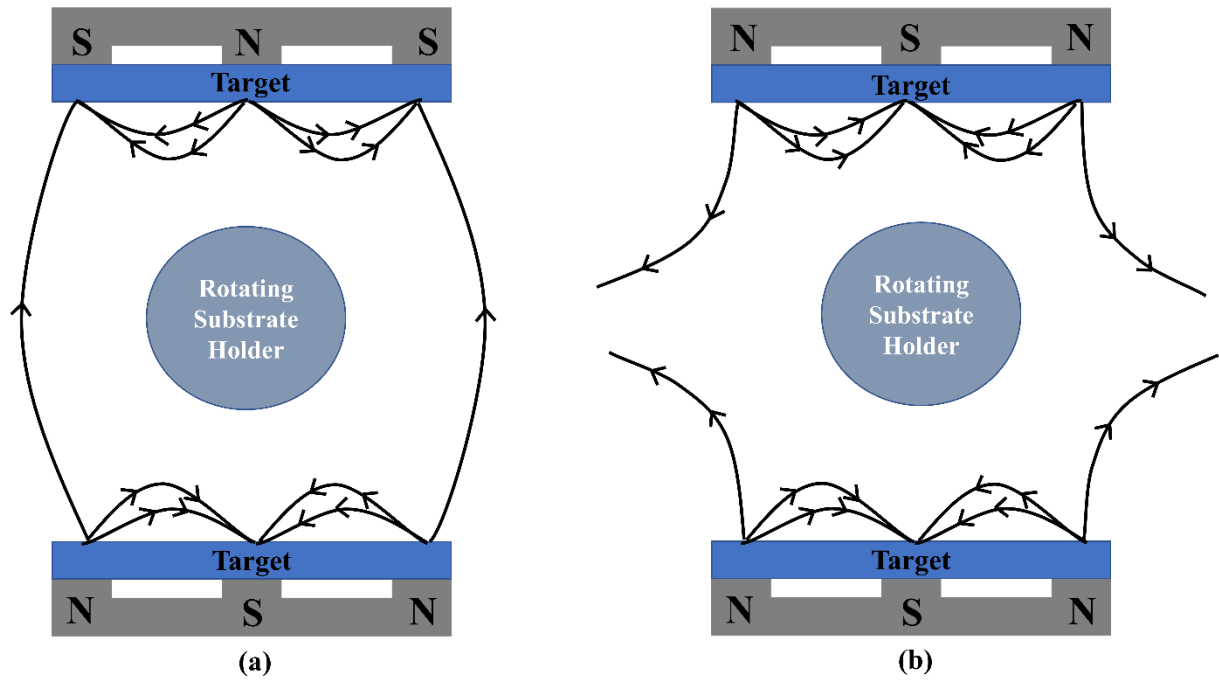


Figure 2.4. Schematic diagram of top view of unbalanced magnetron sputtering systems having (a) closed-field configuration, and (b) mirror-field configuration.

2.4.2. Types of magnetron sputtering on the basis of power source of cathode.

From the discussion in the previous section, it is evident that the unbalanced magnetron sputtering with closed-field configuration forms plasma of high density throughout the sputtering zone. Changing the design of cathodes was not enough to obtain a good coating. Moreover, the unbalanced magnetrons are widely used for industrial purposes and for laboratory-based experiments (where substrate to target distance is small), balanced magnetrons are still being used. Different power supplies for the magnetrons were explored for better sputter yield and dense plasma formation during sputtering.

2.4.2.1 D.C. magnetron sputtering.

In the traditional D.C. magnetron sputtering (DCMS), the cathode is kept at a constant negative voltage. D.C. power source is the most primitive type of power source used in sputtering systems. The working principle of unbalanced and balanced magnetrons in the previous section was discussed on the basis of DCMS only. Positive ions produced in the plasma are driven toward the cathode target, resulting in a vaporisation of atoms and molecules on the target surface as a result of sputtering. The argon gas is generally used as the working gas in DCMS. Commonly operating in the pressure range of 0.1 – 1.5 Pa and an applied cathode voltage in the range of 300 – 700 V, whereas the target surface's magnetic field strength lies in the range of 20 – 60 mTesla. This leads to the current and power densities of 4-60 mA/cm² and 20 – 60 mTesla, respectively. This pressure regime and operation parameters define a collision-free sputter deposition process, where the deposition rate is limited by the target power density, and the sputtered atoms almost maintain their energy of a few eV obtained from the sputtering event [54]. Due to the presence of both electric and magnetic fields, the path of electron in sputtering chamber is quite complicated (**Figure 2.3**). As seen from **Figure 2.3(a)**, the magnetic field is arched, and electrons are reflected back after encountering cathode sheath edge. They keep bouncing back and forth in cycloid like trajectories along the magnetic field lines until they collide. The energetic electrons are locked in this region, which is where the majority of ionisation events occur.

2.4.2.2. Radio frequency magnetron sputtering.

Radio frequency (RF) magnetron sputtering, is a technique that involves alternating the electrical potential of a current in a vacuum environment at radio frequencies to avoid a charge building up on certain types of sputtering target materials (dielectric materials), which over time can result in arcing into the plasma, spewing droplets and causing quality control issues on thin films, or even leading to the complete cessation of atom sputtering, terminating the

process. Traditional DCMS is a low-cost method of coating metal targets that can conduct electricity such as gold. When it comes to dielectric target materials, coatings that are non-conducting insulating materials that can take on a polarised charge, the DCMS fails. Aluminium oxide, silicon oxide, and tantalum oxide are examples of typical dielectric coating materials used in the semiconductor industry.

RF magnetron sputtering uses an energetic wave to ionise an inert gas in a vacuum chamber, similar to DCMS. These high energy ions strike the target material or cathode, which will form the thin film coating, sputtering off atoms as a tiny spray covering the substrate to be coated. Magnets behind the negative cathode trap electrons over the negatively charged target material, preventing them from bombarding the substrate and enabling quicker deposition rates. Positive ions are created over time and accumulate on the target surface, giving it a positive charge. This charge can develop to the point where a complete detachment of sputtering atoms being discharged for coating. The surface of the target material can be cleaned of the accumulated charge with each cycle by alternating the electrical potential with the RF power source. The electrons are attracted towards the target material in the positive cycle, giving it a negative bias. The ion bombardment of the target to be sputtered proceeds in the negative portion of the cycle, which occurs at the radio frequency of 13.56 MHz, which is used internationally for RF power supply equipment. RF magnetron sputtering has several advantages depending on the application. RF plasmas diffuse throughout the chamber rather than concentrating around the cathode or target material as they do with DCMS. At a lower pressure, RF Sputtering can maintain a plasma throughout the chamber. As a result, there are fewer ionised gas collisions, resulting in more efficient line of site for the deposition of coating material.

2.4.2.3. Pulsed D.C. magnetron sputtering.

Various modifications were made over the years to improve magnetron sputtering technology, to increase the plasma density at the substrate, and to allow the deposition of dielectric films. Now the issues of depositing dielectric materials either through a dielectric target or through reactive sputtering with the help of D.C. power supply were addressed. Hence, pulsed D.C. magnetron sputtering (PDCMS) was developed. The asymmetric bipolar pulsed or unipolar pulsed based PDCMS configurations can be used [53,55]. Asymmetric bipolar pulsing was created to solve problems with reactive sputtering. In comparison to conventional DC and RF based systems, the pulsed system has a much wider parameter range, and the pulsing of the discharge allows for much more flexibility due to additional control parameters such as pulse width, duty cycle (the percentage of time that the pulse is on), and pulse frequency. In reactive sputtering, the deposited film on the substrate is a compound which also gets deposited on the target. Therefore, it results in a material of different composition than the bulk target. In case the compound being deposited is an insulator, such as TiO_2 , Al_2O_3 , TiN , etc., then they act as a capacitor. The metal target acting as cathode becomes negatively charged, whereas the plasma facing side of the insulator layer collects a positive charge, which is problematic for various reasons:

- The DC current is unable to conduct through capacitor. The discharge current is primarily carried by positive ions impinging on the target. Hence, relatively few ions will reach the part of the target covered by the insulating compound and sputter the compound, and the area of the target covered by the insulating compound gets poisoned.
- It's possible that the parasitic capacitor won't be able to charge all the way to the discharge voltage. If this is the case, the insulator will break down, resulting in an

abrupt release of charge carriers. It causes the localised current density to rise, forcing the arc discharge regime to emerge, which is undesirable.

- If the insulating film completely covers the cathode, the discharge will be extinguished as soon as the insulator surface voltage falls below the voltage required to keep the discharge going.

The solution for the above problems is to use PDCMS, particularly with bipolar pulsed discharges. In a bipolar pulsed discharge, the accumulated positive charge during the negative voltage pulse gets neutralized by electron bombardment during a positive voltage pulse. Alternatively, RF magnetron sputtering (operated at 13.56 MHz) can be used to deposit dielectric compound layers. RF power source is the sole choice when depositing from thick electrically insulating (often complex) target materials. In comparison to PDCMS, the RF magnetron sputtering can produce high-quality insulating thin films, such as Al₂O₃ from an insulating Al₂O₃ target [56]. However, the deposition rates are in most cases significantly lower. The RF power source can also be utilised to produce aluminium oxide films by reactive sputtering of aluminium. Reactive deposition of aluminium oxide using RF radiation, on the other hand, deposits at just 2–3% of the metal deposition rate [52]. Furthermore, the RF-driven magnetron sputtering devices are very complex systems and also very difficult to scale up for commercial applications.

2.4.2.4. High power impulse magnetron sputtering.

High power impulse magnetron sputtering (HiPIMS), has recently been proposed as one solution to stay below the power limit for target/magnetron damage while achieving a highly ionised flux of the sputtered material [57]. HiPIMS achieves this by using pulsed plasma discharges with peak power densities in the range of 0.5 – 10 kW/cm² (averaged over the target surface) and a low duty cycle in the range of 0.5 – 5 percent, which is far lower than the 50 – 90 percent in the PDCMS mentioned in the previous section. The HiPIMS discharge achieves

peak current densities of up to 3 – 5 A/cm² by delivering square voltage pulses of roughly 500 – 2000 V [58]. With a repetition frequency of 50 – 5000 Hz, the pulse length is in the range of 20 – 500 s, but commonly 30 – 100 s is used for depositing thin films. To distinguish this technology from other pulsed magnetron processes, Anders et al. defined HiPIMS as pulsed magnetron sputtering with a peak power that is typically two orders of magnitude higher than the time-averaged power [59]. One of the key advantages of HiPIMS over the conventional sputtering process is the control over powerful high voltage pulse that ionises a very high proportion of the target material without overheating, creating a thick plasma cloud with virtually no droplets. HiPIMS has enhanced film adhesion and allows more uniform films to be deposited on complex shaped substrates due to the high voltage levels for short periods of time and increased velocity of ionisation of the target coating material. HiPIMS is becoming more used for robust, very high density films with high columnar growth and no voids on substrates where more traditional, line-of-site deposition fails to cover the "Hills and valleys" of irregularly shaped substrates like drills or other cutting tools. The advantages of high-intensity arc technology and magnetron sputtering are combined in the HiPIMS coating. HiPIMS has another benefit of being simple to implement, as any existing Magnetron Sputtering system can be converted to a HiPIMS system with a little retooling. In many circumstances, all that is required is a HiPIMS power supply.

The section 2.2. of PVD coatings gives a comprehensive idea of how the coatings are produced and deposited through PVD technique. Many more techniques are available in market for coatings deposition. Since the work done in the subsequent chapters are majorly related to PVD coatings, a detailed discussion about the PVD coatings and its different variants was necessary. From the next sections, we will discuss the types of coatings reviewed for the work done in subsequent chapters.

2.5. Coatings.

The essential engineering factor is the component surface. The surface of a workpiece is frequently susceptible to wear and corrosion when it is in operation. The intricacy of material tribological properties, and the economic issues of friction and wear, call for more investigation. In developing countries, approximately 30% of energy is lost due to friction. Friction and wear losses are estimated to reach 1 and 2% of the gross domestic product in highly industrialised countries. As a result, there is a growing demand for surface modification techniques that can improve the wear resistance of materials. Unfortunately, there is a large variety of surface treatments to choose from, covering a wide range of thicknesses. The choice must be made so that the surface treatment does not adversely affect the attributes of the substrate for which it was initially selected; for example, it should not lower the load-bearing capabilities of the substrate. This substrate element has been commonly disregarded in surface engineering, with the protective covering receiving far more attention. Similarly, the surface treatment chosen should be appropriate for the task. If a thin protective layer will suffice, it is pointless to focus on processing a thick layer on top of a substrate. It's worth remembering that wear resistance is a quality of systems rather than materials because the workpiece material is continually wearing against something else. The wear resistance of a material in a given construction is determined by its relationship to its surroundings (e.g., lubrication and sliding/rotation speed). Wear is determined, in general, by the interaction of two opposing properties: ductility and hardness. Wear can be decreased by changing the surface layer to become more ductile, allowing for more plastic deformation without the particles breaking off. Soft surface layers (polymeric or solid lubricant layers) can reduce delamination wear significantly. The resistance to abrasion wear, on the other hand, is low. However, by making the surface layer tougher, wear can be decreased. Increased hardness, on the other hand, also entails an increase in the elasticity strain limit and a decrease in ductility, resulting in a

reduction in fatigue resistance and, as a result, brittle failure. The surface engineering procedures to be utilised depend on the system properties (i.e., if the wear is produced by delamination or abrasion). Reduced grain size is an intriguing strategy that could increase mechanical strength and fracture toughness (Hall Patch effect) [27].

2.5.1. Design Criteria.

The design criteria of wear resistant and low friction coatings is divided into two types:

- Structural design.
- Functional design.

The structural design of the coating includes aspects related to the physical, mechanical and chemical architecture of the coating on micro or nano scale (depending on the type of coating).

Some structural design aspects are as follows:

- Grain size.
- Grain morphology and orientation.
- Porosity.
- Crystal structure of each layer.
- Number of individual layers.
- Growth stresses and residual stresses.
- Chemical composition.

The function design parameters are related to the specific mechanical or chemical property of the coating desired by the researchers, such as:

- Hardness.
- Elastic modulus and Poisson's ratio.
- Adhesion.

- Fracture toughness.
- Thermal expansion mismatch with the substrate.
- Chemical stability.
- Thermal stability.
- Overall thickness.

Many of these properties are unknown, highly variable, or extremely difficult to achieve due to the nature of coatings, but they are important contributors to coating's performance. A coating's structural and functional properties are intrinsically linked. The structural and functional qualities of the coating will be influenced by some components of the structural design. The impact of layer design on grain structure, interfacial tension, and growth stress in coatings is the finest example of this. As a result, many of these design elements must be considered simultaneously.

2.5.2. Influence of structural design parameters on functional properties.

The structural design of coatings starts with material selection. According to the material selected, the deposition process is selected for the coating. For soft polymer-based coatings, spray and spin coatings are used. Whereas, for hard ceramic coatings PVD method is used. After this step, the structure and complex composition of coating is decided. The polymer based coatings used for reducing friction and wear are either enforced with nanoparticles, or with other polymeric materials, or both [49,60–62]. However, for the hard ceramic coatings, selection of the type of material bonding (i.e., ionic, metallic, or covalent) is required. As it influences the material's thermal, physical, and mechanical properties. The functional properties like adhesion, modulus of elasticity (E), hardness (H), chemical, and thermal stability are critical indicators of friction and wear performances. The H and E values of the coating is highly influenced by the type of bonding, chemical composition, crystal structure,

and microstructure, such as grain size. The thermal stability depends on the material selection and the type of bonding. Simple polymeric and metallic coatings typically yield better adhesion, but lower hardness. In contrast, the nanocomposite polymeric coatings and hard coatings with ionic or covalent bonds exhibit better hardness, thermal and chemical stability. Therefore, the coating structural design should be tailored to demonstrate all the desired properties.

2.6. Types of coatings.

The three broad types of coating being discussed in present dissertation for ambient and high temperature applications are as follows:

- Hard ceramic coatings.
- Solid lubricant coatings.
- Diamond like carbon (DLC) based coatings.
- Polymer coatings.

The polymeric coatings are generally used for low temperature tribological applications. However, incorporation of thermally stable polymers like polytetrafluoroethylene (PTFE) and polyamide into the metal matrix have shown significant reduction in friction and wear for high temperature applications [63,64]. The hard ceramic coatings and DLC based coatings can be used for ambient and high temperature tribological applications. The structural design of these coatings has been altered many times to get the desired properties. The most widely used structural designs for the above coatings are as follows:

- Monolithic coatings.
- Multilayer coatings.
- Compositionally graded coatings.
- Nanocomposite coatings.

The definitions of all the above-mentioned coating structures have already been discussed in the first chapter. All the coatings being deposited through PVD can be termed as nanostructured (monolithic, multilayer, structurally graded, compositionally graded, and nanocomposite) coatings. Various new applications in high technologies are now possible due to the remarkable physical, mechanical, and chemical capabilities of nanostructured coatings. These exceptional qualities are the result of interface and nanoscale phenomena connected to structural quirks of nanostructured coatings where the volume percentage of the interface phase is unusually high and crystallite size does not surpass 100 nm. A considerable portion of the atoms in a nanostructured coating are generally found at interfaces (grain and interphase borders), where their behaviour differs from that in the bulk. This causes the interface effect to be present. The nanoscale effect happens as a result of the fact that many fundamental solid-state phenomena have length scales of only a few nanometers or less.

2.6.1. Hard Coatings.

The development of hard coatings is one the most successful examples of the lubricant technology paradigm shift from liquid to solid materials. It has almost eliminated the cost of coolant utilization and recirculation in the machining operations. The hard coatings posse's high thermal stability and wear resistant surfaces. The development of hard coatings started with the nitride and carbide based hard monolithic coatings. After it came the development of multilayer and composite coatings. Initially, the architecture and structure of all these coatings were only optimized to achieve peak hardness [65–67]. Whereas, in the recent years these hard coatings have evolved into even more complex composite coatings, having highly complex chemistry and compositions for optimized hardness, toughness, and high temperature resistance [68–78]. Several literature reviews of these materials can be found in the literature [28,79].

Nitrides, carbides, borides, and oxides of transition metals are typically employed in coating materials to tools or hard coatings. TiN, TiAlN, CrN, ZrN, TiSiN, TiAlSiN, CrAlN, and TiAlCrN are nitrides used as coatings for cutting tools; TiC, CrC, and WC are coatings made of carbides [80–84]. Due to its chemical inertness, high hardness, and excellent wear resistance, TiB₂ is used for boride coatings. They can also be placed in tool steel due to its strong adhesive properties [85,86]. These boride coatings are used in machining operations like micro milling, which are characterised by high levels of friction. Al₂O₃ is one of the most often utilised oxide coatings. Diamond-Like Carbon (DLC) is a somewhat less popular coatings for cutting tools [87]. **Figure 2.5** represents the type of bonding present in hard coatings. The coatings with covalent bonding (CN, Si₃N₄, AlN, etc.) possess good hardness and strength, but lack good adhesion to the substrate. The coatings with ionic bonds (Al₂O₃, Cr₂O₃, etc.) possess good thermal stability and chemical inertness, but are brittle in nature. Whereas, the coatings with metallic bonding possess good ductility and adhesion, but lacks hardness. Hence, the choice of coatings depends on the type of application intended.

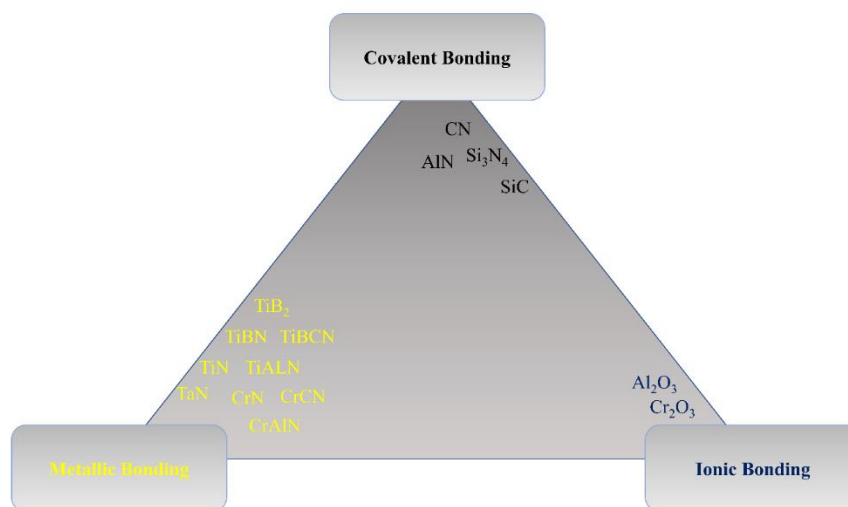


Figure 2.5. Chemical bonding triangle of hard coatings.

Alloying elements like Al, Si, B, C, La, etc. with the basic nitride matrices of Ti and Cr have become a common practice to improve the functional properties of the nitride coatings. Additionally, it was found that doping these elements could reduce the formation of oxide scale at the coating surface, which could be interpreted as improving the coating's resistance to oxidation [88,89]. As an illustration, the oxidation temperature can be increased up to 1000 °C as a result of the creation of a thick and adherent mixed $\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3$ scale and the grain boundary diffusion reduction of Cr and O species brought on by doping a third element [88,90]. Due to the low free energy of production for the oxide of doped elements, an excessive addition of doped elements may worsen oxidation resistance [91,92]. H. Du et al. [93] mentioned that the incorporation of La into the matrix of CrAlN reduces the internal stress of the coatings. The La percentage was varied 0-7 wt% and the microstructure of the coating changed from nanocomposite to multilayer as the concentration of La increased. The addition of La also increased the H/E and H^3/E^2 ratios, which in turn gave good friction and wear properties. Hence the doped element also influences the grain structure of the coating. Several examples of grain refinement of the coating by doping of Cu, Si, Ni, etc. have been reported in the literature [94–96]. All the above nanocomposite coatings contain small amount of nanocrystals dispersed in an amorphous matrix. The segregation of one phase at the grain boundaries of another phase leads to the creation of a nanocomposite structure. The creation of the nanostructure is aided by this action, which inhibits grain expansion. Compared to bulk materials made up of grains that are 5100 nm in size, nanocomposite materials have better and even entirely new properties because to the small grain size (410 nm) and important roles played by grain boundaries. Unique nanocomposite materials can be made by forming nanocrystals with a ceramic, and metallic matrix using a wide range of borides, nitrides, carbides, and oxides [94,97–99].

After the development of nanocomposite structures for hard coatings, researchers also started developing coatings with multilayer architecture. Due to the robust interatomic bonding,

ceramics (transition metal oxides, carbides, and nitrides) are introduced to multilayer systems to offer enough hardness and wear resistance. They also adhere quite well to strong alloys and metal substrates. **Figure 2.5** presents a classification of hard ceramic coatings for wear protection based on their bonding properties. Brittleness and a relatively high coefficient of friction (CoF) (0.3 to 0.8) are disadvantages of hard ceramic coatings [100]. As a result, they are constrained in tribological applications that demand a low CoF by nature. Solid lubricants, or materials with inherently low CoF (below 0.1), are preferable to be used as the top layer to address this problem. Examples include MoS₂, WS₂, PbO, and graphite. Such coatings have relatively low hardness and wear resistance, and will be discussed later in the chapter. For particular tribological applications, the coating materials mentioned above are advantageous. However, by mixing many materials to create a composite or multilayer structure, its performance may be further improved. To achieve superior tribological qualities through the synergistic impacts of various materials, the main idea behind the material selection and design process for multilayer coatings is that the strength of one material should cover the weak property of the other. The design of multilayer coatings in terms of their function and structure, taking into account the material choices for individual layers, interfacial layers, and layer structure in terms of sequence and thickness, enables flexible tailoring of surface attributes (for example, the hardness to elasticity modulus ratio) and performance. Fundamental research has demonstrated that the hardness significantly influences abrasive wear properties to the elastic modulus ratio of coatings [66,88,101]. To avoid early coating failure due to crack propagation and fractures, high toughness should also be guaranteed. Combinations of hard metallic/metallic, metallic/covalent, or metallic/ionic materials can produce coatings with great hardness and toughness. As interfaces in multilayer coatings act as locations of energy dissipation and crack deflection, increasing stability at the coating's interfaces by creating

nanocrystalline or multilayer films may assist in solving these issues. This will increase the coating's overall toughness.

Many signs of progress were made in developing super hard multilayer coatings (hardness > 40 GPa). The superlattice multilayer coating is one of the most examples of super hard coating. Superlattice films, multilayer coatings made of two coherently stacked, alternated materials with periodicity lengths in the nanoscale range, have been reported to have very high hardness values up to a hundred times harder than those of their single-layered constituents. Helmersson et al. [102] reported that the single-crystalline coherent TiN/VN superlattice structure created by physical vapour deposition on single-crystalline MgO (100) substrates, the improvement in hardness was up to 250 percent compared to single-layered materials in the 1980s. Thus, a periodicity length of 5 nm was discovered to correspond to the maximal hardness. A relatively lower hardness was observed by metal superlattices, but the single crystal nitride superlattices experienced very high hardness values like, TiN/CrN [103] (40 GPa hardness), CrN/ZrN [104] (30 GPa hardness), TiAlN/CrN [105] (40 GPa hardness), TiN/ZrN [106] (28 GPa hardness), TaC/SiC [40] (46 GPa hardness), etc. There are different explanations for the increase in the hardness of superlattice coatings. Some model suggests that (a) the difference in elastic modulus between the two layers is required to increase the hardness, and (b) the coherency strain at the interface of the two material has only a limited effect [107]. On the other hand, some researchers suggest that the high hardness is based on the restricted dislocation movement between the coating layers due to the Hall Patch effect [108]. In addition to the high hardness values, bulk and coated engineering components also require a high enough fracture toughness to maintain their integrity. Unfortunately, these material characteristics frequently influence one another, with high strength often implying low fracture toughness and vice versa (particularly for materials exhibiting plastic behaviour). Most superlattice structures also suffer

from high residual stresses [40,106,109,110]. These high residual stresses promote brittle failure during tribotesting and lead to high friction and wear values.

As discussed above, the multilayer coatings with superlattice structure offer high hardness values, but high residual stresses are detrimental. The problem of these high residual stresses was overcome by introducing soft, ductile layers within the hard layers. As thin coatings provide limited resistance to bulk surface deflections, brittle ceramic single layer coatings like TiN would break under the bending pressures caused by the elastic or plastic deformation of nearby soft substrates. The bending stresses increase with coating thickness on a flexible substrate. This is why thick, hard coatings would be unable to shield soft substrate materials from tribological harm effectively. The hard layers can efficiently slide over each other by alternating hard and soft materials, preventing significant bending stress accumulation [85]. The metal "soft" layers serve as shear zones to enable sliding. Internal interfaces can also serve as locations for energy dissipation and crack deflection. In conclusion, multilayer coatings with such alternating properties can combine high hardness with the ability to deformation. In a thick coating, the system acts as a brittle monolith under thick coatings (**Figure 2.6(a)**), with stresses primarily at the top surface. Near the contact circle, where the maximum tensile stresses are present, a near-axisymmetric cone crack indicates the presence of fracture [111]. In thin coating (**Figure 2.6(b)**), the principal maximum in tensile stress changes to the bottom surface of the coating when it starts to flex. Radial cracks begin in the centre region and spread across the contact axis on median planes. Peak tensile stress at the top surface propagates outward from the contact circle onto the shoulders, resulting in secondary ring cracks that are generally shallow in depth [112]. Whereas in thin films (**Figure 2.6(c)**), the maximum tensile stresses return to the top surface near the contact circle as cracking is inhibited in the compression zone beneath the Hertzian contact. The membrane stresses then increasingly come into the equation [113]. Conservative relations can be obtained by assuming that fracture occurs

when the Hertzian stresses, the flexural (bending) stresses, or the thin film tensile stresses exceed coating strength, despite the complexity of the detailed fracture mechanics occurring because of the above three reasons.

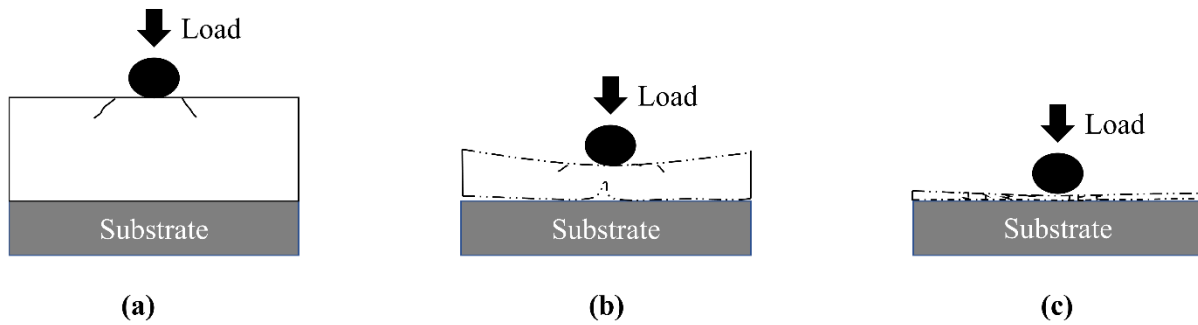


Figure 2.6. Schematics of bilayer structure and deformation regimes of a brittle layer on a thick compliant substrate under axisymmetric indentation (a) thick coating, (b) thin coating, and (c) thin films (reproduced from reference [114])

Lackner et al. [114] studied the micro- and nanoscale investigation of deformation in multilayer coatings on the model system Ti/TiN. The 1 μm thick Ti/TiN coating containing bilayers of different modulation periods and different modulation ratios performed better than the single layer TiN coating. The columnar growth structures in the deposited TiN single layer coatings exhibit microcracks as a result of the high levels of stress present in the coatings. The stress level in multi-layer coatings was significantly lower, and no fracture was seen in the layers as they were being deposited. The coating with bilayer period of 62 nm and modulation ratio of 1:1 showed highest hardness, attributed to the Hall Patch strengthening mechanism. Ring-like fractures emerge around spherical indentations in TiN single layer coatings, whereas edge-like cracks and deformation are detected in multilayer coatings, caused by shear deformation of Ti layers and brittle fracture of the TiN layers. Below these fissures or deformation bands, the soft austenite substrate frequently contains shear steps. The ratio of the brittle to soft phase dictates how the deformation bands and cracks themselves form. The deformation bands and fissures are more perpendicular to the coated surface at larger modulation ratios, where TiN content is

more. The multilayer coatings also possessed good antiwear properties and excellent adhesion to the substrate. Diego et al. [115] coated Ti/TiN and TiAl/TiAlN coatings on austempered ductile iron substrates. The TiAl/TiAlN coating possessed better hardness, but the Ti/TiN coating showed good adhesion strength due to low residual stresses. The coatings were tested under rolling contact fatigue tests, and the Ti/TiN coating showed significant reduction in rolling contact fatigue wear. The reduction in the rolling contact fatigue was attributed to the lower mismatch in mechanical properties of substrate and the Ti/TiN coating than TiAl/TiAlN coating. Caicedo et al. [116] deposited Ti/TiN, Zr/ZrN and TiN/ZrN coating on AISI 5160 steel. The mechanical properties were enhanced with the multilayer architecture. The coatings showed better hardness than what was expected from the rule of mixtures. TiN/ZrN coating having both layers as the ceramic hard layers showed greater hardness. However, the relatively softer Ti/TiN and Zr/ZrN coatings showed good scratch resistance as the microcracks being formed at vicinity of the top surface was easily able to change its direction as it penetrated deep inside the coating on contact with the ductile metal layer, which was not possible in TiN/ZrN coatings containing both layers of brittle nature.

For high temperature applications, both nanocomposite and multilayer architecture has been used for hard coatings. Al, Cr, Si, B, and other elements that produce oxide and nitride were included to the hard coating compositions to provide oxidation protective surface layers because tool coating developers understood the significance of high temperature oxidation protection from the beginning. For instance, single phase TiN coatings, whose structure control with ion bombardment was thoroughly studied by Petrov et al. [117], have developed into a broad spectrum of oxidation resistant hard coatings where TiN is the primary component, examples include TiAlN, TiAlCrN, TiAlBN, TiAlSiN, TiAlBSiN, TiN-Si₃N₄, TiN-TiB₂, and other examples [118–124]. In the recent advancements, these nitride based coatings are also doped with vanadium, molybdenum, or other Magneli phase oxides [125], which are lubricious

at high temperatures. Therefore, the research for high temperature hard coatings is not only limited to creating coatings with superior thermal resistance, but also creating coatings which can adapt to high temperature conditions. The left side of **Figure 2.7** shows a schematic representation of temperature adaptable chameleon behaviour, which involves the intricate chemical, physical, and structural evolution of the contact surfaces. These evolutions are self-directed toward establishing of low friction and wear contact conditions for effective adaptive behaviour. In the recent years, several key tactics were used to accomplish this:

- Diffusion of metal lubricants to the surface at high temperatures.
- Formation of lubricious oxides at high temperatures.
- Temperature and strain actuated structural evolutions in the contact.



Figure 2.7. Schematic representation of chameleon adaptive coatings. Reprinted with permission from reference [126].

2.6.1.1. Adaptive mechanism using metal diffusion.

Silver and gold are dependable solid lubricants used in air and vacuum applications [127]. They perform best when applied to a hard supporting substrate and display poor shear strength throughout a temperature range spanning from below ambient to their melting point. To benefit from the above-described solid lubrication with noble metals while maintaining wear resistance, hard nanocomposite coatings were created. Binary yttria stabilized zirconia (YSZ) and gold (Au) nanocomposite coating materials showed high hardness (15 GPa) with additions of up to 20 atomic% (at. %) of gold [128]. High ductility and fracture resistance were displayed by coatings containing 10–20 at. % Au. Micron-sized grains of Au were visible on the surface of YSZ-Au coatings in this compositional range when they were heated to temperatures of 500 °C, creating a low-shear interface on a hard surface that could handle the imposed contact load and a lower CoF. When sliding in air against a sapphire counterpart, these films offered friction coefficients of approximately 0.2–0.4 from room temperature to 500 °C. This is consistent with the friction performance of noble-metal lubricants on hard substrates. After high temperature testing, studies of the YSZ-Au composite coating structure showed that microscopic amounts of noble metals spontaneously coalesce at the coating surface to enable macroscopic lubrication. Other studies with noble metals as nanoscopic inclusions include YSZ/Ag [129], Cr₂AlC/Ag [130], TiC/Ag [131], CrN/Ag [132], etc. When tested in the 25–500 °C temperature range for sliding in air against a wide range of counterpart materials, including steel, alumina, silicon nitride, nickel-chromium based superalloy, and diamond, these studies of Ag-lubricated hard coatings showed friction coefficients between 0.2 and 0.4 for 10–20 at. % Ag additions. Because the thickness of the film changes (sometimes significantly) as the Au or Ag coalesces at the surface and is sometimes not reported in these investigations of temperature-adaptive coating materials, it is difficult to estimate the wear rate of such materials. **Figure 2.8** represents

the schematics of Ag or Au diffusion from the nitride or oxide matrix onto the surface of the coating at high temperatures.

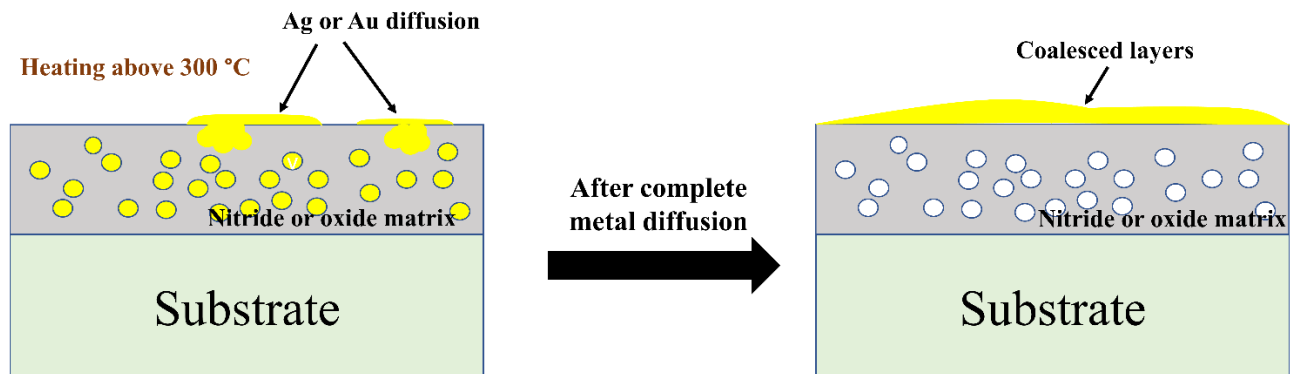


Figure 2.8. Schematics of Ag and Au diffusion onto the surface of the coating at high temperatures.

At temperatures above 300 °C, all of the silver-based lubricants also develop lubricious double oxides, which provide the high temperature oxide adaption mechanism. YSZ-Mo-Ag nanocomposite coating was developed, which forms lubricious oxides of silver molybdate at high temperatures [133]. Since the diffusion of noble metals to the surface of coating is very fast at temperatures above 300 °C, no operative lubrication mechanism is present on the surface once the noble metal layer wears off. To control the rapid diffusion of noble metals. A diffusion boundary of TiN was introduced the nanocomposite architecture [133]. A multilayer coating was developed with two adaptive YSZ-Mo-Ag layers and a 300 nm thick TiN layer separating the adaptive layers. Just like the single monolithic coating of YSZ-Ag, the top adaptive layer in this coating was also susceptible to a single irreversible change. After cooling down, the top layered wore out within 50 cycles. Hence exposing a different chemically homogenous adaptive layer buried underneath the diffusion barrier (TiN layer). As a result of this exposure, silver diffused laterally beneath the TiN diffusion barrier layer to the area where wear was occurring, lubricating hundreds of sliding cycles.

2.6.1.2. Adaptive mechanism using tribo-oxidation.

Tribo-oxidation is the primary mechanism in this class of materials that causes a decrease in CoF. Binary oxides are formed by transition metal nitrides, such as VN, MoN, and WN, and are lubricious at high temperatures [75,134–138]. An Erdemir crystal-chemical model [100], established a correlation of these oxides CoF with their ionic potential. In the oxides with high ionic potential, the cations are heavily shielded with the anions and the oxides formed have a low melting point. The heavily shielded cations can also not interact with other cations, making them easy to shear. On the contrary, the oxides with low ionic potentials are strong, stiff, and hard to shear even at high temperatures, as their cations keep interacting with other cations forming strong covalent bonds. Considering aerospace bearing systems, Peterson et al. [114] conducted the first systematic experimental examination of many binary and ternary metal oxide lubricants for high-temperature sliding Inconel X-750 alloy surfaces with applied oxide powders. MoO₃ was found in this study to lower CoF to roughly 0.2 at 700 °C tests, among other prospective oxides. The defect structure linked to the formation of substoichiometric compounds, also known as Magnéli phases and named for the Swedish scientist Arne Magnéli who first determined the structure of these compounds in molybdenum and tungsten oxides, is thought to be responsible for the lubricious nature of transition metal binary oxides. For instance, Mitterer and Hovsepian et al. [26,139–141] reported that vanadium and vanadium nitride can be strategically added to the conventional TiAlN tool coating compositions to minimise CoF at temperatures of 700 °C and higher with the creation of substoichiometric VO_{2-x} and a low melting point V₂O₅.

2.6.1.3. Adaptive mechanisms using structural transitions.

For the evolution of structural surfaces, surfaces can be repeatedly stressed in sliding and rolling interactions as well as subjected to temperature cycling. One such case is the reorientation of polycrystalline hexagonal lubricant solids (MoS₂, WS₂, WSe₂, graphite, etc.)

that were initially randomly oriented, and their surface transforms from amorphous to crystalline to produce contact surfaces with hexagonal basal planes that are parallel to the surface [142–146]. This results in a significant reduction in friction and wear because these easily sheared planes offer low friction surfaces that are also resistant to oxidation. Even in conditions of room temperature, the reorientation is visible. The results showed that from an initially poorly crystallized and randomly orientated material, few monolayer thick and highly (002) oriented hexagonal layers are swiftly produced at the contact surface (**Figure 9**) [147]. A few monolayer thick hexagonal WS₂ tribofilms with extremely low coefficients of friction (CoF) for sliding in humid air against steel balls were reported by Gustavsson et al. [148] for totally amorphous W-S-N coatings. This was accomplished by friction-induced surface structure transformation. The rate of wear substantially decreases after such ultra-low-friction hexagonal surface layers are produced. For some of the MoS₂ based adaptive chameleon coating formulations evaluated under temperature fluctuations from -80 to 180 °C, Hamilton et al. [149] observed wear rates of $2 \times 10^{-8} \text{ mm}^3\text{N}^{-1}\text{m}^{-1}$. This study found that temperature had a significant impact on sliding behaviour for coatings with extremely low wear rates, which was linked to nearly frictionless relative slip (CoF of 0.02-0.04 in self-mated sliding contacts) of hexagonal basal planes at temperatures above -50 °C.

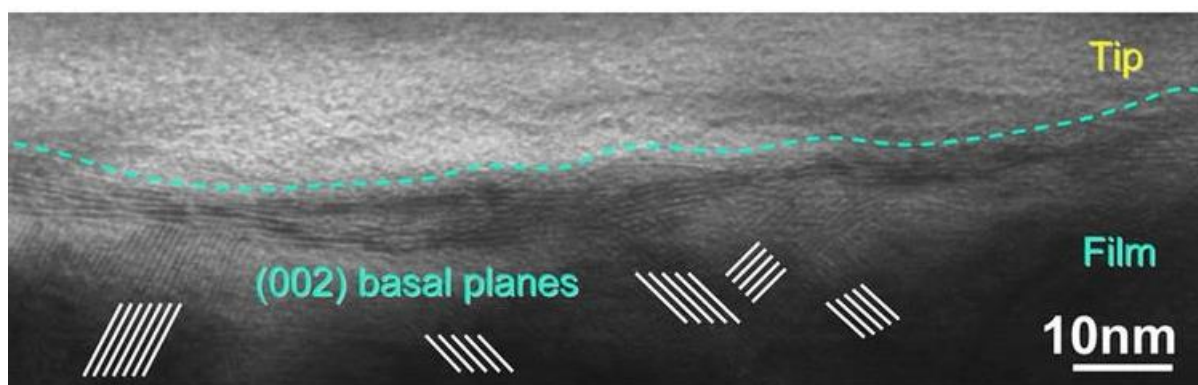


Figure 2.9. Example of friction induced re-orientation and crystallization in W-Mo-Se-S composite coating after a thousand cycles of sliding against SiC fiber tip at room temperature. Reprinted with permission from reference [147].

2.6.2. Solid lubricant coating.

The solid lubricant coating contains the nanostructured coatings DLC, transition metal dichalcogenides, soft noble metals, and polymeric compounds. The inclusion of soft noble metals as solid lubricants in the matrix of hard coatings as already been discussed in the previous section. Although the DLC and polymer-based coatings come under the class of solid lubricant coatings, they form entirely new sets of coatings and require special attention, which will be discussed later. The coatings discussed under this section are nanostructured coatings based on transition metal dichalcogenides. MoS₂ and WS₂ are well recognised for their solid lubricating action and are frequently used in various applications among the many members of the transition metal dichalcogenide family of compounds. Their inter-mechanical weakness, which is inherent to their crystal structure, is what causes their lubricating tendency. MoS₂ crystallises in a hexagonal form, much like graphite, with a sheet of molybdenum atoms sandwiched between two sulphur layers that are hexagonally packed. The covalent bonds in the S-Mo-S sandwich are held together by weak Van der Waals forces, which leads to mechanical weakness between the lamellae. As a result, the basal planes move over one another by intracrystalline slip when subjected to shearing stress. Therefore, the development of (002) basal planes and subsequent reorientation parallel to the direction of sliding, as well as (b) the development of a transfer layer on the counterface to allow interfacial sliding, are the major mechanisms for imparting minimal interfacial shear in the transition metal dichalcogenides based coating [150]. When used in dry inert gas or an ultrahigh vacuum, both MoS₂ and WS₂ coatings exhibit extremely low CoF ($\mu \sim 0.05$ or less) and long wear lives (millions of sliding cycles), preventing oxidation and reactions from in a humid environment and maintaining their inherent solid lubrication [151,152]. However, sliding in humid air results in higher CoF (0.15-0.2) and incredibly short wear life (typically less than a few hundred cycles). This is most likely

because dangling or unsaturated bonds on the edge of basal planes react with the moisture and oxygen in the environment to form tribo-oxidation products, such as MoO_3 (MoO_3 is only lubricious around $300\text{ }^\circ\text{C}$) and WO_3 [152]. Because MoS_2 and WS_2 can create transfer films on the counterface, covering just one of the sliding couple surfaces would be sufficient to produce low friction after the initial run-in phase. Furthermore, the desirable crystallographic texture of (002) basal planes parallel to the sliding direction or fully crystalline transition metal dichalcogenide coatings are not required to be present at the beginning. Numerous experimental studies have demonstrated that frictional stresses can cause MoS_2 -based coatings that initially lack long-range order to crystallise or cause crystalline coatings that have already been deposited to reorient their (002) planes parallel to the sliding direction [127,153].

Doping of noble metals in the transition metal dichalcogenide matrix has also been explored as solid lubricant coatings for aerospace applications. Lince et al. [153] studied the effect of addition of Au in the MoS_2 matrix, with Au at. % varying from 42- 100 % under low and high contact stresses. The films with the best performance (lowest CoF and highest endurance) at high contact stresses had lower Au contents (i.e., 42 and 59 at. % Au). However, Films with high Au content (i.e., 75 and 89 at. % Au) worked well at low contact stress. The findings point towards potential mechanisms for enhanced performance with different compositions were: low Au content offers the best film characteristics for high contact stresses while yet guaranteeing that enough MoS_2 is accessible at the sliding contact; higher Au concentration restricts the quantity and size of MoS_2 particles that are transferred to the opposing surface at low contact stresses, creating the ideal transfer layer for effective lubrication. The transition metal dichalcogenide based coatings, provide good lubrication properties, but they don't possess good load-bearing properties (due to low hardness) and wear out easily under high stresses

2.6.3. DLC based coatings

In order to create coatings with superior wear resistance, corrosion resistance, high thermal conductivity, and dampening capacity, researchers are currently concentrating on coatings made up of diamond-like carbon (DLC)[154–163] and graphite-like carbon (GLC) [23,164–166]. DLC is a mixture of carbon allotropes of the sp^2 and sp^3 hybridizations. Amorphous carbon coating has demonstrated excellent adhesion and friction resistance, which may be used to construct lubricant-free sheet metal processes [145]. Numerous studies have been conducted recently to improve the wear performance of coating materials based on carbon. According to research, the most important factors affecting friction and wear resistance are temperature, sliding speed, applied load, humidity, and sliding distance. Therefore, optimal test conditions are necessary to optimise and improve friction and wear behaviour. DLC film has excellent biocompatibility, chemical inertness, impermeability, hardness, scratch resistance, and anti-wear and anti-sticking properties [167–171].

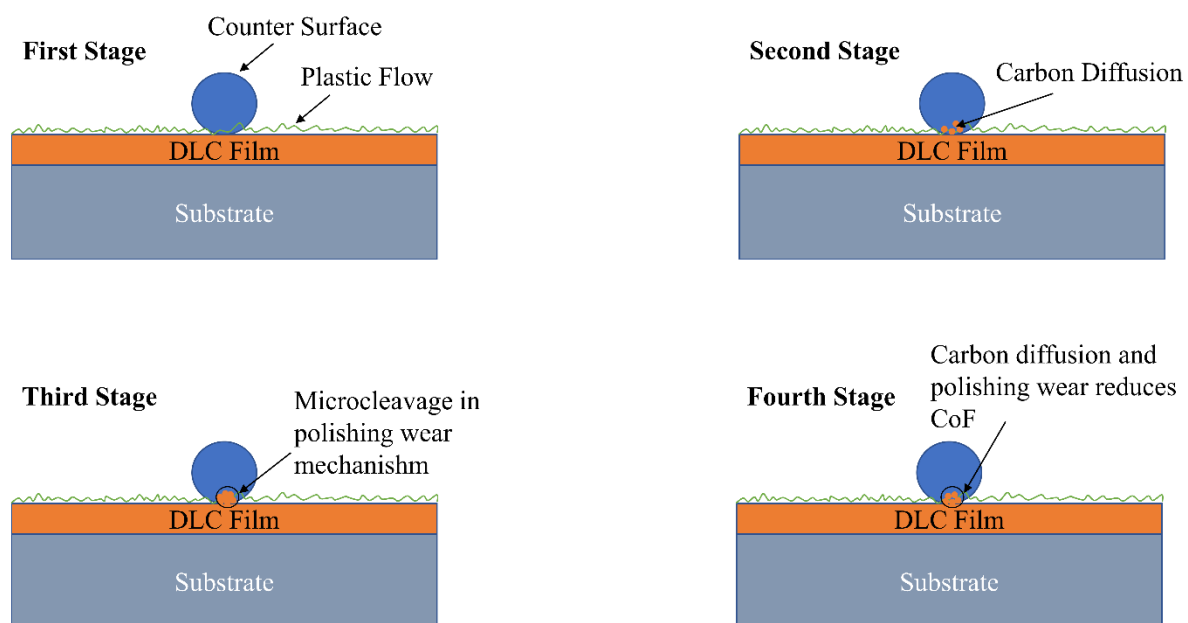


Figure 2.10. Schematics of wear mechanism in DLC coatings.

Several processes are engaged in the wear process. However, due to the impacts of carbon diffusion on the wear process, researchers think that polishing wear and abrasive wear are the

critical mechanisms involved in the DLC surface film. According to **Figure 2.10** and the explanations following, the wear mechanism involves four distinct stages:

- First stage: Due to the applied load, asperities in the DLC/CNTs film attempt to pierce the softer counter surface, which finally leads to plastic flow of material around the coated surface.
- Second stage: Plugging of the counter surface by coated asperities leads to abrasive wear because of increased temperature and frictional forces. Micro-cleavage is caused by the coated surface asperities, which becomes weaker as carbon diffusion increases.
- Third stage: The strength of the atomic bond is decreased more by carbon diffusion, than by frictional forces, leading to micro-cleavage in polishing wear. As a result, the CoF of coating surface and roughness are reduced.
- Fourth stage: Continued carbon diffusion growth indicates weakened coated layer, increased smoothness, and decreased CoF. CoF is stabilised as a result of the counter surface's increased tensile strength and coating's improved smoothness.

Besides the above mentioned mechanisms, the film thickness, tribochemistry, and the interaction of film with the environment also plays an important role in influencing friction and wear. DLC/GLC/CrN coatings on stainless steel were studied by Li et al. [172] under various environmental conditions. Due to the greater thickness, hardness, highest adhesion strength, and greater roughness, the CrN coating exhibited the best load-carrying ability in the atmosphere. A combination of abrasive wear, oxidative wear, adhesion wear, and peeling off causes CrN coatings to fail. The graphitization of the transfer film, dense structure, and low surface roughness led to better tribological characteristics and the best load carrying ability of GLC coatings when compared to other coatings under distilled water. At lower loads DLC showed better results than GLC and CrN, but the thickness of DLC limits the load carrying capacity of the coating. DLC based coatings come under particular class of materials, which

can have high hardness and possess good lubrication properties at the same time. The high hardness of DLC films limits the thickness due to presence of high internal stresses [173]. Itzel et al. [174] doped W and Mo into the amorphous DLC matrix to relieve internal stresses. The doped W and Mo formed onion like structures in the nanocomposite matrix. The DLC coating showed lower CoF and wear under tribotesting with the load of 2N. Aboua et al. [175] demonstrate that as temperature increased from 80 °C to 100 °C, COF value decreased from 0.0521 to 0.0314, respectively. The main wear mechanisms are polishing and abrasive wear due to carbon diffusion on the DLC surface coating.

Deposition of DLC coatings can either be done from a graphite target or by creating a plasma of methane and argon gas. The DLC deposited through the graphite target is non-hydrogenated, while the DLC deposited through the plasma of methane and argon gas is hydrogenated. The hydrogen free DLC shows lower values of CoF and wear in air or humid environment. In contrast, the hydrogenated DLC shows lower values of CoF and wear in vacuum [176–179]. The dangling sigma bonds present in hydrogenated DLC interacts with the water molecules in humid environment and leads to increase in CoF and wear. Since the thickness has been one of the major concerns for DLC, Mahboubi et al. [180] deposited multilayer N-DLC/DLC on steel substrates. The presence of C-N bonds diminishes the interlink connections that connect the carbon networks, which lowers the coating's hardness and internal stress. The N-DLC/DLC coating also had C-H peak in addition to the C-N peak. According to Raman and XPS spectroscopy results, the total number of sp^2 carbon bonds increases with nitrogen incorporation in the DLC coatings. The increase in total sp^2 bonds makes the coating more adherent to the substrate and lowers its hardness. The creation of C-N (sp^2) bonds was found to be crucial to the growth of overall sp^2 carbon bonds. The two-layer coating demonstrated outstanding tribological behaviour with great stability and low friction coefficient. The DLC coating, the second layer, has a low coefficient of friction. Whereas, the coating's adequate

adherence to the substrate is present in the first layer (N-DLC coating). Compared to single layer coatings, the wear attributes of the double layer N-DLC/DLC coating were much better. Optimal mechanical and tribological properties, as well as optimal adhesion between the coating and the substrate, were attained with the deposition of the multilayer N-DLC/DLC coating.

The ratio of sp^3 to sp^2 hybridized carbon determines the hardness, wear resistance and elastic modulus of DLC films. However, at high temperatures, DLC films go through processes like oxidation, graphitization, dehydrogenation, and lose their ability to lubricate. Sometimes they even start to peel away from the substrate. As a result, a transfer layer and wear debris build on the counterparts. DLC films quickly peel off over 300°C , resulting in their shorter wear lifetimes [55,181,182]. In contrast to the majority of the aforementioned nanocomposite coatings, many materials exhibit low friction at high temperatures primarily as a result of the creation of their oxides. In contrast, DLC exhibits low friction at high temperatures primarily as a result of graphitization. The structural changes of DLC at elevated temperatures were investigated by Wang et al. [183] from the standpoint of structure origin, they discovered that high temperatures encourage graphitization and accelerate the production of graphene nanoscroll. They found that when the temperature reaches 150°C , debris contains graphene nanoscrolls with a spherical shape. CoF was lowered to 0.012 thanks to a fine balance between graphitization and nanocrimping. This equilibrium was upset when the temperature reached 200°C , which raised the CoF. Doping elements in DLC matrix to increase the thermal stability has been extensively studied. Si-doped DLC films were examined by Zhang et al. [184]. (Si-DLC). It was discovered that the doping of Si might improve thermal stability by inhibiting graphitization at high temperatures in addition to hardness and bond strength. The author also ascribed Si-DLC's low friction at high temperature to the material's improved thermal stability and the development of a lubricant layer comprising Si on the worn tracks' surfaces. In the

study of the Ti/W co-doped DLC films on steel, Grigoriev et al. [185] found that the elements reduced the sp^3 concentration and created chemical interactions with carbon atoms, which was beneficial in lowering the CoF.

Generally speaking, a few micrometres of film thickness are sufficient to increase the durability of DLC films in tribological applications at high temperatures [178]. But in these circumstances, more inherent stress from compression is produced, which encourages the breakdown of film adhesion and peeling from the substrate surface [186,187]. In particular, spontaneous debonding occurs when DLC films are placed over a metal alloy because of the low chemical affinity, or poor chemical bonding, of the DLC films with the substrate. The thermal stability of DLC films can therefore be increased through the use of a strong film/substrate bonding force. Depositing the interlayer between the substrate and DLC films is now a successful procedure [188]. In particular, the silicon-containing interlayer has a chemical affinity for the alloy's metal atoms and the carbon atoms that make up the DLC films, making it more chemically compatible with the material system under study.

system under study.

DLC has a variety of outstanding mechanical qualities and can keep its properties throughout a pretty wide temperature range, which gives it a wide range of industrial applications. The adhesion is a crucial component for the use of DLC films on components, such as those in engines and on tools, in a dry and unlubricated environment [189]. As was already indicated, adding an intermediate layer, such as one containing chromium, can create a Cr-C bond or prepare a gradient layer, both of which greatly aid in improving adhesion [169,170]. DLC films have also been employed as a solid lubricant in water hydraulic systems because of their great chemical stability and wear resistance in the aqueous environment, and their stable performance between 50 – 200 °C [190,191]. A lot of research work is still being done to

improve the performance of DLC in harsh environments, and many more applications of DLC coating will also be seen in future.

2.6.4. Polymer coatings.

The interfacial properties of solid materials can be modified by polymer coatings, which also make the surfaces corrosion-resistant, self-cleaning, self-healing, and water/oil releasing [192]. Additionally, polymer coatings with low shear strength can offer an extremely low coefficient of friction and wear under specialised or strictly regulated test settings due to their strong self-lubricity and wear resistance. Self-lubricating polymer coatings are preferred in applications because they feature a mix of characteristics that are not present in other solid lubricating coatings, like, weight, cost, and corrosion resistance [193]. Self-lubricating polymer coatings, however, have numerous drawbacks. They have less wear resistance, more wear debris, and a shorter lifespan than hard coatings like ceramic coatings and carbon-based coatings. The coatings are prone to softening and failing at high temperatures due to their low heat resistance and low thermal conductivity. Furthermore, the environment significantly influences how well they perform tribologically. Due to the surface's chemical interaction with its surroundings, a worn surface may have different chemistries, microstructures, and crystallographic textures from the coating as a whole. It might not be possible to create extremely low friction and a long wear life in a different environment [194]. For some applications, oxidation- and age-related degradation also poses a challenge. By fully utilising the advantages of two or more components, combining materials with various qualities is an efficient way to improve the properties of the combined material, and the properties of the material can be adjusted and improved. In order to enhance the performance of polymer coatings, functional fillers have been used. These fillers offer a stable and low coefficient of friction, high thermal conductivity and heat resistance, enhanced mechanical properties for higher loads, and optimised adhesion between the coating and substrate.

An overview of common polymer matrices, filler types, and individual filler materials are shown in **Figure 2.11**. Upon reviewing the literature, it was discovered that the following polymer materials are frequently used as lubrication coating matrices: phenolic resin (PF), epoxy resin (EP), poly(*p*-hydroxybenzoic acid) (PHBA), aromatic thermosetting copolyester (ATSP), polyimide (PI), polyurethane (PU), polyamide-imide (PAI), polyamide (PA), polyether-etherketone (PEEK), polytetrafluorethylene (PTFE), polyoxymethylene (POM), ultra-high molecular weight polyethylene (UHMWPE), and polyphenylene sulphide (PPS). The application of a single polymer as a lubricating coating is always subject to some limitations. For instance, PTFE [195] has a high wear rate and easily creeps despite having great thermal stability, chemical inertness, and a very low coefficient of friction. Although PI [196] is a high-performance engineering plastic with outstanding mechanical capabilities, high creep resistance, and high temperature resistance, its use in lubrication is constrained by its high friction coefficient. PPS [197] resists high temperatures well. However, due to its intrinsic brittleness and poor impact strength, it is not ideal for applications that must withstand rigorous operating conditions, such as bearings and sliding components, despite having high corrosion resistance, radiation resistance, and chemical resistance. The well-known characteristics of PU [198] include its exceptional abrasion resistance, corrosion resistance, high flexibility, strong adhesion to surfaces, ability to customise its properties, as well as some other unique qualities, yet they have very low thermal stability. To overcome the drawbacks of single polymer materials, additional materials, such as fillers, are added to enhance the mechanical and tribological characteristics.

The fillers which are added to the polymer can be characterized into reinforcing and lubricating fillers. The mechanical properties of polymer composites can be improved by reinforcing fillers, which are materials with greater strength and elastic modulus than the polymer matrix. A sizable portion of the literature uses fibres and nanoparticles as reinforcing fillers. Carbon,

glass, and silicon fibres are traditional reinforcing fibres [199,200]. Carbon nanotubes are also suitable for strengthening polymer composite materials due to their one-dimensional structure similar to fibres and great strength [180,182].

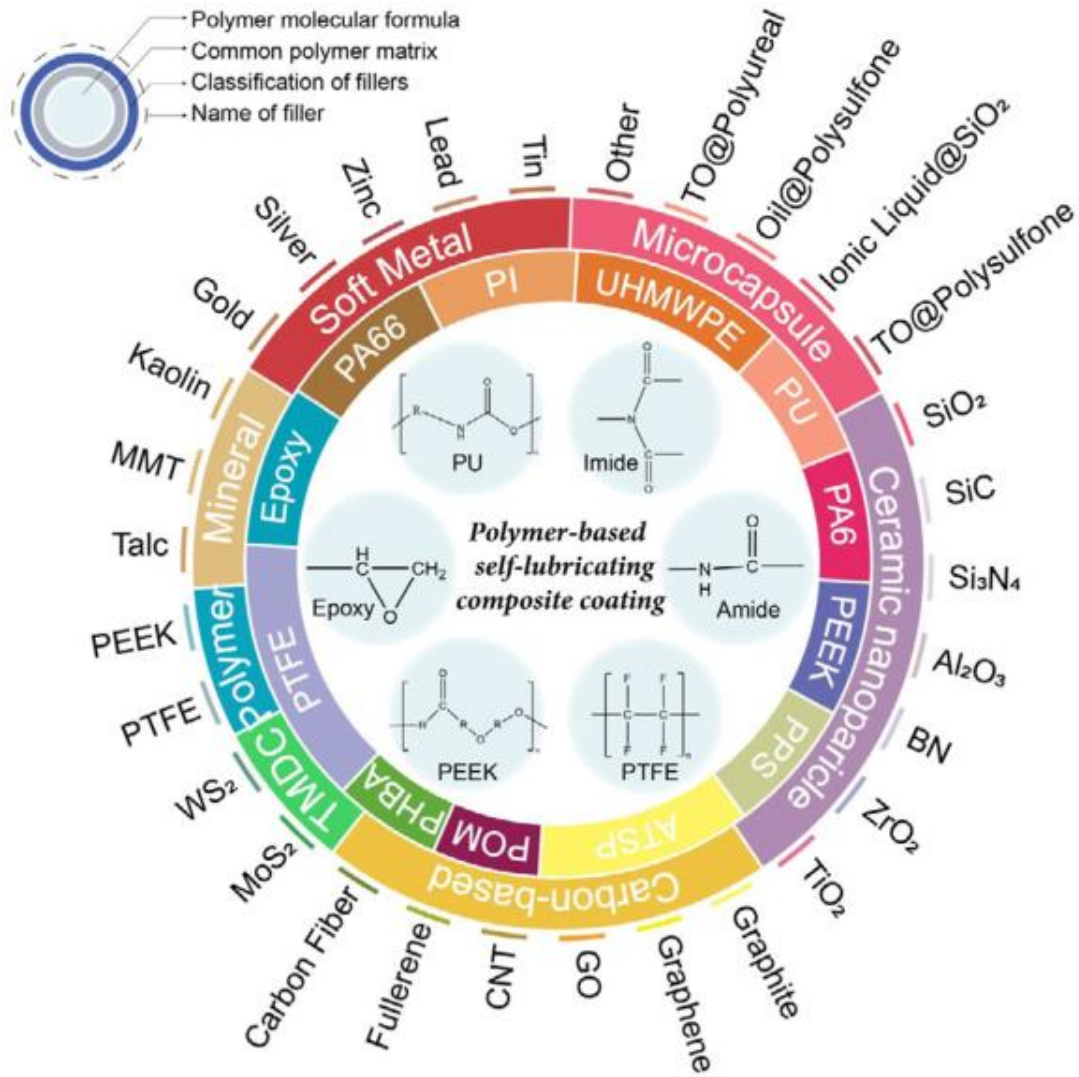


Figure 2.11. Common polymer coatings with filler elements. Reprinted from open access reference [201].

Al₂O₃, SiO₂, SiC, and ZnO are a few examples of the nearly all sorts of nanoparticles that can be employed as a reinforcement phase for polymer-based composites. Functional substances that lower the friction coefficient of polymer composite materials are known as lubricating

fillers. Polytetrafluorethylene, graphite, graphene, MoS₂, black phosphorus, gold, and copper are the major lubricating fillers. Some reinforcing fillers can efficiently increase the mechanical strength and friction characteristics of polymers. For instance, silica and short carbon fibres added to an epoxy resin significantly improve the resin's ability to reduce friction [202]. The tribological characteristics of PA6 have been enhanced by the use of carbon nanotubes [203]. Additionally, the friction can be efficiently reduced by the rolling bearing effect of the nanoparticles in the friction process [204]. High strength materials like graphene also helps in enhancing mechanical and lubricating properties of the polymer [205].

Due to its significant tribological applications and proven friction reduction and anti-wear capabilities, the carbon nanoparticles have generated a lot of interest. Fullerenes, graphene, carbon nanotubes (CNTs), and nanodiamonds are four typical carbon nanomaterials used in coatings to improve anti-wear and reduce friction [206,207]. Large carbon cage molecules seen in fullerene, a graphene-based substance, are thought to be zero-dimensional (0D) analogues of benzene. Due to its spherical shape, strong intramolecular nature, and weak intermolecular bonding, its lubricating action is of great interest [208]. With a Young's modulus of 1 TPa and a tensile strength of up to 100 GPa, graphene is very strong and robust [183,197,205,209]. It is frequently used to improve the tribological and mechanical qualities of the polymer matrix because of its layered structure, which encourages effective lubrication. Nanodiamonds have outstanding mechanical qualities and a very low surface roughness, which are important for the self-mated tribosystems' friction and wear behaviours [210]. In addition, black phosphorus, is a newly developed two-dimensional lubricating and strengthening filler. Because of their layered structure, transition metal dichalcogenides, particularly MoS₂ and WS₂ are effective lubricants for lowering the CoF and wear rate of the polymer matrix [211,212]. Yongcai et al. [46] fabricated superhydrophobic PU nanocomposite coatings with the addition of micro sized MoS₂ sheets. Insertion of micro sized MoS₂ resulted in reduction of CoF, but

no significant effect was observed on the abrasion resistance across various concentrations of the nanosheets.

From the above cited literature, it is obvious that the addition of fillers in the coatings helps in enhancing the friction reducing and antiwear properties of the polymer coatings. The use of reinforcing fillers improves the coatings' toughness via fracture bridging and filler extraction, shear yielding, and crack deflection, as well as the coatings' strength through efficient stress transfer and the enhancement of the polymer interfacial layer. The layered and oxidized nanosheets/nanoparticles can lead to significant reduction in CoF, that's why they are termed as lubricating fillers. However, before using any type of filler for the polymer matrix, one must understand the mechanism behind the enhancement of tribological properties with the filler under consideration.

2.7. Methodology of coating selection.

The study and application of tribological coatings have a long history, yet there is still no straightforward general guideline to guide the choice of tribological coatings. In general, it is considered that determining the wear mechanism was one of the most crucial aspects of coating selection, as we must first determine the true cause of surface failure before determining which coating is required. However, in most cases, the rubbing process transforms different wear mechanisms into one another, and occasionally they even happen at the same time. **Figure 2.12** gives a schematic overview of interaction of different wear mechanisms. Therefore, it becomes challenging to select a coating depending on the wear mechanism to counter. The tribological performance is a result of the entire tribological system and is not an inherent quality of the materials. The tribological performance in coating systems is affected by a severalfactors from 5 aspects: the counterpart (roughness, hardness, elasticity, fracture toughness, chemical properties), the coating (influenced by a deposition process and parameters), the substrate

(roughness, hardness, elasticity, thermal properties), the solicitation (load, kinematic condition, contact geometry), and the running environment (temperature, humidity, lubrication). Hence finding a general method for coating selection from the literature, databases, or bench tests is extremely difficult because any modification in a parameter may result in a significant difference in tribological performance.

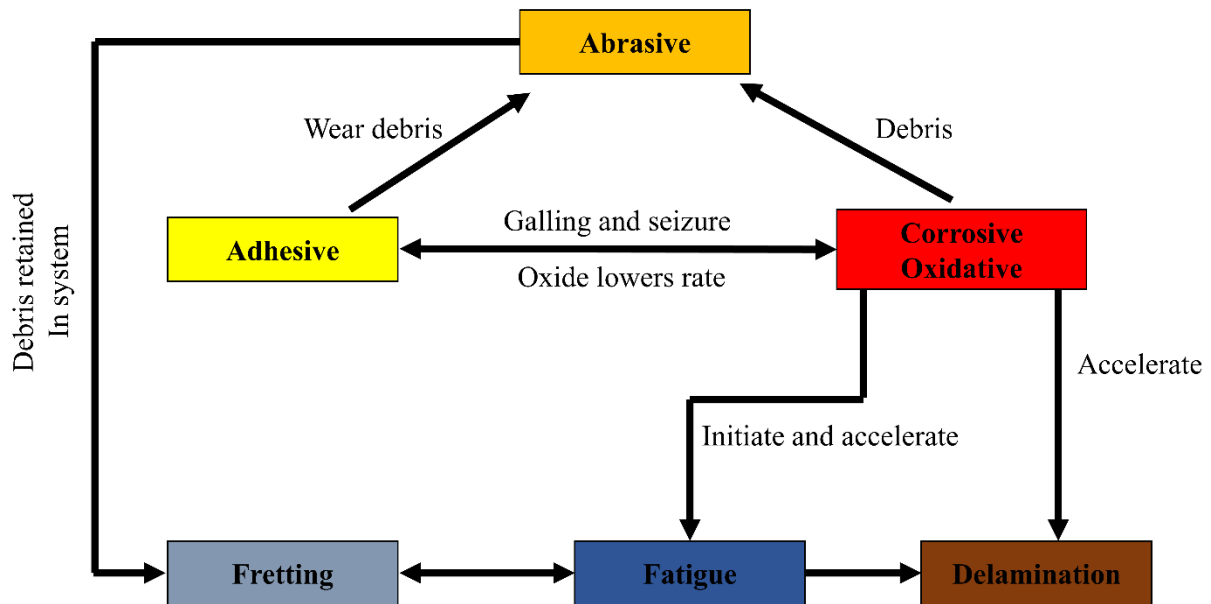


Figure 2.12. Wear mechanisms generally occurring in a system.

According to the abovementioned issues, the wear mechanism cannot be determined with any degree of certainty, and a variety of factors affect tribological performance. Therefore, simulation experiments to determine the tribological performance of coatings must be conducted in order to identify the best coating for a particular application. However, time-consuming tribological studies are unable to measure all of the possible coatings. Based on the application of the coating, a systematic pre-selection is needed.

2.7.1. Coating pre-selection.

The pre-selection process is lengthy as it informs collecting information from literature and industries to select the coating material. Pre-selection of coatings is the process of matching

coating properties (the deposition method and the coating material) with the needs and constraints of the tribological application. The process of matching should take into account the following factors. **Figure 2.13** represents the coating pre-selection process.

Criteria based on the deposition method:

- The deposition technique must be appropriate for the substrate. The substrate material must allow for the deposition process. For instance, the deposition temperature should be lower than the substrate material's maximum withstand able temperature (except laser cladding and welding).
- The substrate's geometry must be accommodated by the deposition process. The substrate's size shouldn't be larger than what the deposition device can handle. The deposition technique should avoid using a lot of stop-off medium for selective deposition. The substrate's shape should be compatible with the deposition method's throwing capacity.
- The required criteria of coating thickness should be satisfied. Depending on the application, a coating thickness may be anticipated. The range of coating thicknesses that can be achieved using the chosen techniques should include the desired value. The deposition technique for thin coatings should allow for accurate and uniform thickness control.
- The deposition process should give coatings and substrates a strong enough adhesion. The prerequisite for effective wear resistance is adequate substrate-coating bonding strength. The deposition process (the bonding mechanism) determines the bonding strength, which is further determined by materials of the substrate and coating, coating thickness, and deposition parameters (temperature, substrate bias voltage, gas pressure, etc.).

- Porosity, residual stresses, and topography specifications for coatings should be met. One might anticipate a dense or porous coating depending on the application. The chosen deposition technique must guarantee that the deposited coatings can achieve the necessary requirements. Due to the high deposition temperature and varying thermal expansion of the coating and substrate, different deposition procedures might produce different residual strains at the interface between the coating and the substrate.

Criteria based on coatings:

- The substrate material must suit the coating materials. The relationships between the coating material and the substrate material require consideration of a wide range of factors. The ability to put the coating material on the substrate material is the first requirement (sometimes with the use of an intermediate layer). Second, the elastic modulus of thin hard coatings should be comparable to that of the substrate. Third, the coating material's thermal performance in high temperature applications must match the substrate.
- The coating's materials must complement the counterpart. To prevent adhesive wear, the coating material should be physically and chemically distinct from the counterpart material. It is advantageous to use coatings that can create a low friction transfer film with the counterface. To avoid abrasive wear, the counterface's hardness difference from the coating shouldn't be too high.
- The coatings must adhere to tribological standards. The criteria for coating qualities can be converted from the tribological requirements, such as friction and wear resistance.

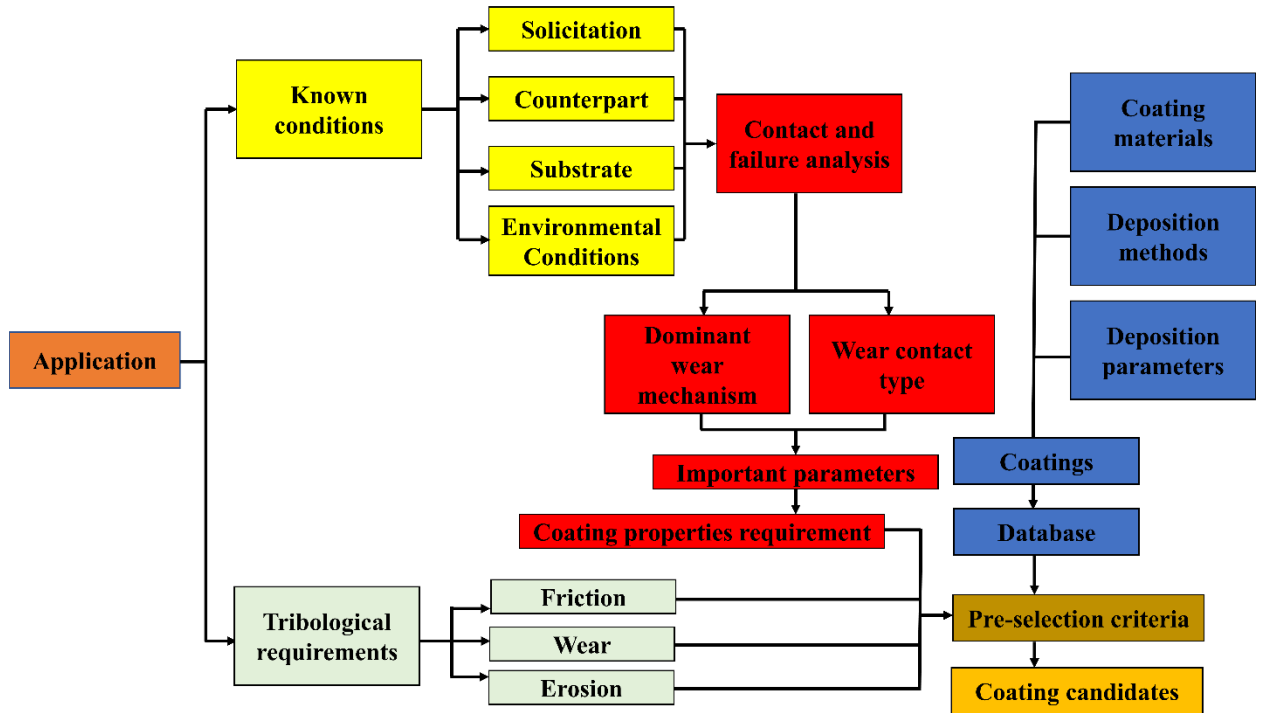


Figure 2.13. Process of coating pre-selection.

2.7.2. Basic characterization of coatings.

The candidates of the coatings from the pre-selection phase must be further explored through simulation or characterization tests to determine the best one and make sure it satisfies the requirements. The type of simulation experiment (hardness, fracture toughness, roughness, elastic modulus, chemical composition, thickness) must be decided upon before the tests. After the testing, it is important to think about how to interpret the results and identify the best coating, especially since coatings might be advantageous in a variety of ways.

After the basic characterization and coating selection, the coating can proceed for tribological testing. In terms of the test results, it is usually simple to determine which coating is the best. Although each coating has pros and cons, in some circumstances the tribological performances of coatings are relatively similar. It is necessary to take a complete approach that balances the coating qualities and the application's needs.

2.8. Problem formulation.

The detailed, in-depth review of the different types of coatings show the following research gaps:

- A higher coating thickness ensures extensive lifespan of the coated tool. Due to the high internal stresses in the hard nitride-based coatings, a higher thickness of the coating cannot be achieved.
- Few studies have mentioned the multilayer coating architecture of Ti/TiN coating containing Ti and TiN layers, having thickness in nanometres.
- The literature available for HiPIMS deposited DLC coating is also very few in numbers.
- Just like the nitride-based coatings, DLC coatings are also not able to achieve high thickness due to internal stresses present in the coating.
- No studies have been done on the galling resistance of DLC coatings based on new ASTM standards.
- High temperature galling studies of the coating has also not been reported in the literature.
- Various types of polymer composite coatings have been surveyed in the literature, but no studies are available for polymer based coatings for enhancing the anti-galling properties at room temperature.

2.8.1. Motivation.

The TiN, DLC and polymer-based coatings have shown good tribological properties across various applications. A higher coating thickness has always been a major concern for hard TiN and DLC coatings. A multilayer architecture containing hard and soft layers could lead to a coating of higher thickness. Moreover, the coatings deposited through HiPIMS have

remarkable mechanical properties. Therefore it is imperative to study the tribological properties of HiPIMS deposited coatings.

Galling has been considered one of the worst kinds of wear, as it results in seizure of machine parts. At high temperatures, the material's mechanical properties decrease, leading to galling at very low loads. The solid lubricant coatings can help prevent galling by reducing adhesive wear. Therefore, the study of galling characteristics of solid lubricant coating is needed at ambient and high temperatures. Since the preparation of PVD coatings is expensive, and difficult to produce. Cost effective coatings were also needed to be explored for protecting the machine tools from galling. Hence polymer composite coatings were also explored.

2.8.2. Problem definition.

In the last two decades, enormous amount of research has been done in the field of coating technology. The development of multilayer and nanocomposite coating architecture has set new benchmarks for coatings operating at ambient and high temperatures. The polymers coatings have also seen a lot of progress, and have been used for various tribological purposes. The requirement of thick coatings for different tribological purposes has led to the development of many types of architecture, which researchers have reported. The authors have tried a new kind of multilayer architecture for the multilayer Ti/TiN coatings in the present study. Since very few or no research is available for the galling characteristics of the coatings as per new ASTM standards, new solid lubricant coatings were also needed to be developed to enhance the galling resistance of machine tools in dry lubrication conditions. So the following queries may arise:

- Whether the new multilayer architecture help in getting coating of high thickness?
- What will be the tribological response of the new coating system at ambient and high temperatures?

- How the solid lubricant coating behaves in galling tests?
- How will the galling behaviour will change with respect to the temperature?
- What will be the structural and chemical changes in the newly developed coating at high temperature operations?
- What will be the galling behaviour of readily available polymer coating?
- How will the behaviour change with the nanoparticle addition in the polymer composite coating?

The present study explores all these queries through systematic and detailed experimental assessment. Hence, the objectives of the present study are outlined accordingly.

2.9. Objectives of work.

The objectives of the present work are as follows:

- Explore the tribological properties of novel multilayer Ti/TiN coatings under lubricated and dry conditions at ambient and elevated temperatures.
- Understand the changes in the tribological properties at ambient and elevated temperatures under lubricated and dry conditions.
- Development of DLC based multilayer coating with HiPIMS.
- Chemical and mechanical characterisation of the coatings developed through HiPIMS.
- Study of friction and wear properties of developed DLC based coatings.
- To Investigate the galling properties of DLC based coatings at ambient and high temperatures.
- To understand the mechanism of the DLC based coatings in improving galling resistance at ambient and high temperatures.
- To explore the cost effective and readily available polymer coatings for their friction, wear and galling behaviour.

- To enhance the tribological properties of the polymer coatings by enforcing them with nanoparticles.