

LITERATURE REVIEW

This chapter begins with a brief descriptions of phenomenon of wear, its different types, factors that affect wear and lubrication (both liquid and solid). It is followed by a note on the necessity of solid lubrication including a brief description of different solid lubricants. An extensive survey on various techniques used for deposition of wear resistant coatings with special emphasis on the importance of thermal spraying process, the requirements for the plasma spraying and key process parameters which affect the microstructure and the quality of coatings is also included in the chapter. The chapter also contains a brief elucidation of high temperature wear of materials. A comprehensive review of literature pertaining to elevated temperature tribological behavior of the composites and coatings containing solid lubricants coatings also forms a part of the chapter. The formulation of the problem is presented at the end of chapter.

2.1 TRIBOLOGY

Most machine components operate under conditions that involve relative motion between two surfaces. Efficient operation and robust performance of these machine components are highly dependent on *tribology* which is defined as the science and technology of interacting surfaces in relative motion (Bhushan, 2013) and encompasses the areas of friction, wear and lubrication of surfaces in relative motion under applied load (Sahoo, 2005). Friction is a common phenomenon that is encountered

in people's daily lives and in most of the industrial applications. The control of friction helps in reducing energy loss and improving the efficiency of a machine (Phakatkar et al., 2009). Wear of material from a surface can lead to severe damage and failure of the component and/or the machine (Ludema, 1996). Friction is the main cause of wear and energy dissipation, and according to Liu et al. (2019) about 1/2 to 1/3 of the world's energy is consumed in various forms of friction. It is obvious that enormous amount of the world's resources are wasted in overcoming friction in one form or another. Lubrication (solid or fluid) is an effective means of controlling wear and reducing friction. Hence, for the survival of a machine, wear and friction must either be reduced or controlled (Bhushan, 2013). The most common approach to reduce friction and minimize wear and catastrophic failure of machine elements or the machine itself is by a proper selection of materials, lubricants and surface modification techniques.

2.2 WEAR AND TYPES OF WEAR

Wear is associated to the interactions between surfaces and more precisely, the removal and deformation of a material on a surface as a result of the mechanical action of the opposite surface as indicated by Rabinowicz (1995). The progressive loss of substance from the operating surface of a body occurring as a consequence of the interfacial rubbing process is called wear (Ramesh et al., 1991). Wear may be classified on the basis of appearance of the worn parts or mechanisms and conditions, which prevail during material removal. The types of wear classified according to the wear mechanisms and conditions are: (i) adhesive wear (ii) abrasive wear (iii) erosive wear (iv) impact wear (v) fatigue wear (vi) corrosive wear.

Adhesive wear is associated with low sliding velocity, small load and smooth surfaces. This is a universal type of wear that can occur in every machine and hard to be eliminated but can only be reduced. Adhesion processes involve the interaction of asperities on two opposing surfaces in relative motion. When the asperities come in close contact, they may weld together, forming a bond at the junction, which has rupture strength greater than the yield strength of one of the contacting solids. In such a case fracture may take place in one of the asperities resulting in the transfer of material from one contacting body to other. **Abrasive wear** occurs when two surfaces, one of which is harder and rougher than the other, are in sliding contact. Abrasive wear is the removal or the displacement of material from one surface by the harder asperities of another surface or by harder, loose particles. This type of wear is dangerous because it can occur suddenly with the introduction of a contaminant and may lead to high wear rates and extensive damage to the surface. **Erosive wear** is a combined process of repeated deformation and cutting. When a solid surface is gradually worn away by the action of fluids and particles, it is called erosion. Erosion of materials can take place under four different conditions: (1) impingement of solid particles against a solid surface, (2) impingement of liquid droplets against a solid surface, (3) flow of hot gases over a solid surface and (4) cavitation at a solid surface in liquid media. The most important form of erosion is that caused by solid particle impingement. **Impact wear** arises from the repetitive impact of two surfaces, which differs from the impact of solid particles on a surface causing erosive wear. **Fatigue wear** refers to the cyclically repeated imposition of a stress state on the surface of a component, inducing a small degree of mechanical damage in the surface and subsurface regions with each stress pulse. Ultimately, the damage accumulation leads to failure by deformation and/or fracture at the surface. **Corrosive wear** is the synergistic effect of chemical reaction at a surface with any of the mechanical wear mechanisms. In

a corrosive environment, sliding surface experience corrosive wear. However, in some cases, the reaction layer protects the surface or even act as a lubricant.

Archard's law describes the inverse relationship between the wear volume loss (W) and hardness (H), which can be expressed as:

$$W = k \frac{LS}{H} \quad (2.1)$$

Where, W , k , L , S and H represent the wear volume loss, wear coefficient, normal load, sliding distance and hardness of softer materials, respectively. (Archard, 1953).

2.2.1 FACTORS AFFECTING WEAR

When two nominally flat surfaces are brought in contact by applying a **normal load**, they touch each other at the tips of asperities only. Hence the real area of contact is much less compared to the apparent area of contact (Archard, 1980). The small regions where the contacting surfaces are close together, are referred to as "junctions" and the sum of the areas of all the junctions constitute the real area of contact, A_r . The total interfacial area, consisting both of real area of contact, A_r , and those regions which appear as if contact might have been made there (but was not) is taken as the apparent area of contact, A_a . The numbers, size and distance of separation of junctions play a dominant role in influencing the friction and wear behaviour of materials in sliding contact.

According to Rabinowicz (1965), when the deformation of the asperity is plastic in a single asperity contact, the real area of contact is directly proportional to normal load and is given by the equation:

$$A_r = \frac{L}{H} \quad (2.2)$$

Where, L is the average load and H is the initial hardness of the softer of the two materials in contact.

Holm (1958) and Bowden and Tabor (1954) have shown that the limiting value of the pressure at the contacting interface is set by the hardness of the softer of the two materials and the real area of contact is given by the above equation. Further, it has been concluded by them that the real area of contact is independent of the surface topography and the apparent area of contact. Hence, load plays an important role on wear of materials. In general, there is a significant increase in wear rate, when load increases from lower to higher value. In general, when graduation in load, the friction coefficient also enhances and rate of wear also rises, as wear is directly proportional to frictional force. There is no general trend with respect to the load. **Contact area** also plays an important role in defining the wear rate of contacting bodies. The contact area is inversely proportional with wear. When the surface has only point contact with abrasive particles, friction coefficient value is high and wear is more. When the contact area is more, then the friction coefficient value is less and the wear rate is lower. **Lubrication** is another dominating factor and plays a major role in controlling the wear. Wear is highly reliant on the lubrication mechanism. Lubrication is a powerful method by which wear in many moving system can be reduced. Solid lubricants such as Ag, MoS₂, graphite, hBN and metal oxides (WO_x, NiO, MoO₃, VO_y, PbO, B₂O₃, MoO₂, ZnO, Re₂O₇, TiO₂, CuO-MoO₂, NiO-MoO₂, PbO-B₂O₃, CuO-Re₂O₇ (Erdemir et al., 2000)) are used to provide lubrication by solid lubrication mechanism. Lubrication is nothing but a means to create a low shear strength film between two mating surfaces and thus avoid the direct contact of the mating surfaces. **The environment** also affects the wear behavior. Environmental

conditions affects the wear of material up to great extent. Wear is less in wet conditions as compared to dry conditions. In moist conditions, moisture plays role of lubrication, hence reduces the frictional value and decreases the wear rate. In dry conditions, the frictional force is higher and enhances the wear of materials. **Counter material** properties have a great effect on the wear of the material. When the hardness of counter surface material is more and surface finish is poor than substrate material (work-piece), then the rate of wear of counter surface will be less and the substrate material will deteriorate more. The abrasive particles of counter material are with more hardness, as abrasive particles easily penetrate the material, while working and the wear rate will be more of substrate material. **Microstructure** also plays an important role in determining the wear of materials. When microstructure is coarse, hardness is less and wear rate is higher. When microstructure is fine, hardness is more and wear rate is on lower side. **Sliding velocity** affects the rate of frictional energy dissipation, and hence the temperature at the sliding interface. So, wear also affected by the sliding velocity.

2.3 LUBRICATION

Lubrication is the control of friction and wear by the introduction of a friction-reducing film between moving surfaces in contact. The lubricant used can be a fluid, solid, or plastic substance. The main function of the lubrication is to reduce the friction and prevent wear apart from protection of the equipment from corrosion. It also controls the temperature by dissipating the heat generated due to the continuous relative motion of assemblies, minimizes the contamination helps in transmitting power (hydraulics). The various types of lubrication mechanisms, i.e. liquid, solid, semi-solid, gases, are available to meet the various challenges being faced due to technological advancements.

2.3.1 LIQUID LUBRICATION

The liquid lubrication is used to control the friction and to dissipate the excessive heat from the system for preventing the wear. The lubricating fluids must have the capability to remove the heat developed from the friction and the abrasion of wear particles away from the load-carrying zone as soon as it is formed. Mineral oil or synthetic oils are mostly used as the liquid lubricant. Cameron (1981) discussed various mechanisms which are used to provide the lubrication between two contacting surfaces; such as **hydrodynamic lubrication**, where the sliding surfaces are separated by a thick film of lubrication due to pressure of the fluid lubricant. The normal load is supported by the pressure generated hydrodynamically by this thick film lubricant. If the contacting surfaces involve the line or point contact, i.e. gear teeth, cam and follower, ball on disc then the local pressure is much higher at the point of contact in comparison to hydrodynamic lubrication. Under these circumstances the dependence of lubricant viscosity on pressure also plays a vital role in providing the efficient lubrication. Lubrication under such circumstances is termed as **Elasto-hydrodynamic lubrication (EHL)**. However, under very high contact pressures, or very low sliding speeds, the hydrodynamic forces are insufficient to maintain even a thin EHL film between the mating pair and in those circumstances, the **boundary lubrication** mechanism is said to provide the sufficient lubrication. Boundary lubricants act by forming adsorbed molecular films on the surfaces; repulsive forces between the films then carry much of the load, and intimate contact between unprotected asperities, with associated adhesion and junction growth, is prevented or limited.

However, liquid lubricants have limitations that hinder their use in certain conditions. They cannot be used in certain applications because of the difficulty in

applying them, sealing problems, weight or other factors. At high temperatures, liquid lubricants decompose or oxidize, become less viscous and their performance gets deteriorated, whereas under corrosive environments liquid lubricants are contaminated, which is not the case in most solid lubricants.

2.3.2 SOLID LUBRICATION

A solid lubricant (self-lubricating) is generally defined as a material that gives lubrication under essentially dry conditions, to two surfaces in contact moving relative to each other. Solid lubricants are generally used in the composite coatings and in composites to provide effective lubrication in such conditions where the liquid lubricants do not provide effective lubrication, i.e. high or cryogenic temperatures, vacuum, radiation and extreme contact pressure as indicated by Furlan et al. (2018).

Graphite and MoS₂ have been widely used as solid lubricants in composites (Wu et al., 2000) to improve their tribological performance. The most widely used inorganic solid lubricants in industry are graphite, boron nitride, and MoS₂ because of their easy-shearing lamellar structure that results in low COF. The hexagonal boron nitride (hBN) has been used in many different anti-wear applications (Carrapichano et al., 2002; Yi et al., 2006; and Skoop et al., 1995). Sulphides, selenides and tellurides (chalcogenides) of molybdenum, tungsten, niobium, tantalum, titanium (e.g. WS₂, MoSe₂, TaSe₂, TiTe₂), monochalcenides (GaS, GaSe, SnSe), chlorides of cadmium, cobalt, lead, cerium, zirconium (e.g. CdCl₂, CoCl₂, PbCl₂, CeF₃, PbI₂) and also some borates (e.g. Na₂B₄O₇) and sulfates (Ag₂SO₄) have also been shown to behave as solid lubricants (Prajapati et al., 2018). Other solid lubricants include noble metals (Au, Pt, and Cu). Due to low shear strength and high plasticity some soft metals possess lubrication

properties, i.e. lead (Pb), tin (Sn), bismuth (Bi), indium (In), cadmium (Cd), and silver (Ag). Silver has been shown to possess effective lubricating capacity over a wide range of temperatures (Guo et al., 2017) and has been used over the years with other lubricants to achieve the self-lubricating properties in the broad range of temperatures. Silver has the capability to lessen the friction and wear and delivers exceptional lubricating performance in low-temperature regime ($< 500\text{ }^{\circ}\text{C}$) during sliding action owing to low shearing capability and high diffusion coefficient (Kong et al., 2014). Inorganic fluorides (LiF , CaF_2 , CeF_3 and BaF_2 (Sloney et al., 1975 and Murator et al., 2009)) and a few metal oxides (WO_x , NiO , MoO_3 , VO_y , PbO , B_2O_3 , MoO_2 , ZnO , Re_2O_7 , TiO_2 , CuO-MoO_2 , NiO-Mo_2 , $\text{PbO-B}_2\text{O}_3$, $\text{CuO-Re}_2\text{O}_7$ (Erdemir et al., 2000)) have also been shown to work as a solid lubricant. Polytetrafluoroethylene (PTFE) and Polychlorofluoroethylene are the examples of organic solid lubricants with polymeric molecules.

2.3.3 NEED FOR SOLID LUBRICATION

Due to advancement in technology, many critical parts of the moving assemblies have to work continuously under conditions of load, speed, temperature and environment. Keeping in view the requirements and challenges of modern-day technology the use of solid lubricants is the only viable alternative to reduce friction in many harsh environments, especially those that include temperatures above $350\text{ }^{\circ}\text{C}$ since liquid lubricants degrade rapidly under these conditions. Dai et al., (2016) reported that liquid lubricants, polymer lubricants lose their lubrication property as the temperature reaches above $350\text{ }^{\circ}\text{C}$ and conventional solid lubricants like graphite and MoS_2 also do not provide effective lubrication above $500\text{ }^{\circ}\text{C}$. Likewise, in food processing units where the liquid lubricants cannot be used to avoid the contamination, or in space where liquid lubricant may get vaporize, in heavy loading conditions, inaccessible locations, in high

dust or lint areas, in intermittent loading conditions as indicated by Zhu et al. (2019), solid lubrication may be the only feasible solution. Several industrial applications such as turbine engine parts, aerospace, automotive engines, cutting tools require low friction coefficient, high wear resistance and anti-oxidation properties (Ouyang et al., 2005). Since, it is not possible to obtain the above-mentioned properties by using bulk monolithic material (Wang et al., 2002), so attention is being focused on solid lubricating wear-resistant composites or composite coatings to solve such problems. High-temperature lubrication involves various industrial applications such as automotive, aerospace and military industries (Torres et al., 2018). High-temperature lubricants possess some characteristic properties which are helpful in diminishing friction and wear between continuously moving contacting pairs at elevated temperature (Chien et al., 2019).

2.4 TECHNIQUES TO FABRICATE WEAR RESISTANT COATINGS

There are number of surface modification techniques available in the market and utilized in the industries, but only a few of them are most effective and applicable, including physical vapor deposition (PVD), chemical vapor deposition (CVD), micro-arc oxidation (MAO), sol-gel, thermal spray, and polymer coatings (Fotovvati et al., 2019). An overview of such technologies is presented below Fig. 2.1.

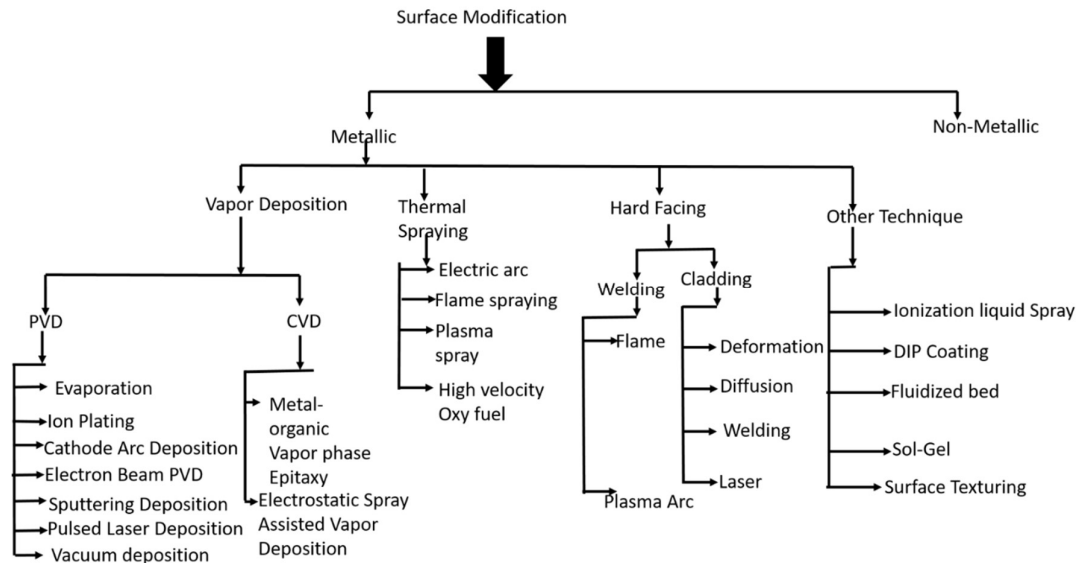


Fig. 2.1 Summarized plot of surface modification techniques.

Physical Vapor Deposition (PVD): The process involves the condensation of vapors in the ultra-high vacuum condition. It is extremely versatile and provides the flexibility in terms of deposition of materials, virtually any metal, ceramic, intermetallic or other compounds which do not undergo dissociation can be easily deposited onto any sort of substrates material, i.e. metals, ceramics, plastics or even paper. PVD coating can be used in many applications such as aerospace, automotive, biomedical instruments, optics, firearms, decorative, and microelectronics. The rate of coating deposition is very low. PVD coatings have high temperature, and good impact strength, excellent abrasion resistance and therefore have the excellent durability. PVD is further classified in number of sub-methods which are used to deposit thin coatings. In **Evaporative deposition** the coating material is vaporized by heating to a temperature of about 1000 - 2000 °C in a vacuum. The substrate is also pre-heated to a temperature of about 200 - 1600 °C. Atoms in the form of vapor travel in straight lines from the coating source towards the substrate where condensation takes place to result in a coating. However, the coatings produced by

evaporation are not desirable for tribological applications as these have poor adhesion with the substrate in comparison to other vacuum-based coatings. **Ion plating** also termed as ion-assisted deposition (IAD) or ion vapor deposition (IVD) process in which the phenomenon 'glow discharge' is utilized. The process of ion-plating involves the concept of thermal evaporation of the coating material and ionization of the vapor due to the presence of a strong electric field and a previously ionized gas, usually argon. The argon and metal vapor ions are rapidly accelerated towards the substrate surface, impacting it with a large amount of energy and gets embedded in the substrate to form a coating. In **Cathodic arc deposition** technique, the high-power electric arc is used to vaporize the material from the cathodic target material which subsequently condenses on the substrate, whereas in **Electron beam physical vapor deposition** method, the target anode is heated to a high vapor pressure by the continuous bombardment of electrons in "high" vacuum and the vapor of target material is transported by diffusion and thus deposited by condensation on the (cooler) workpiece. In **Pulsed laser deposition** technique, a high-power laser strikes the target material inside a vacuum chamber ablating the material from the target and converts it into the vapor which gets deposited on the substrate. **Sputter deposition** technique is based on dislodging and ejecting the atoms from the target material by bombardment of high-energy ions of reactive gases, usually argon. In sputtering the coating material is not evaporated and instead, ionized argon gas is used to dislodge individual atoms of the coating substance. The substrate is placed in front of the target so that it captures the flux of dislodged atoms. Therefore the coating material arrives at the substrate with far less energy than in ion-plating resulting in formation of a distinct boundary between film and substrate. The atoms condense very rapidly after reaching the substrate. The condensation process is crucial to coating quality and may result in a porous crystal structure with poor wear resistance, if not optimized by the

appropriate selection of coating rate, argon gas pressure and bias voltage. In **Pulsed electron deposition** a highly energetic pulsed electron beam ablates the material from the target thus generating a plasma stream under non-equilibrium conditions, while in **Vacuum deposition** technique the deposition of material occurs either atom-by-atom or molecule-by-molecule on a solid surface.

Chemical Vapor Deposition (CVD): In this process the vapor of coating material, formed by volatilization from either a liquid or a solid substance, is forced to flow by a pressure difference or the action of the carrier gas toward the substrate surface. Normally a reactant gas or other material in vapour phase is added to produce a coating of metallic compound. The coating is obtained either by thermal decomposition or chemical reaction (with gas or vapour) near the atmospheric pressure. The chemical reactions usually take place in the temperature range between 150 – 2200 °C at pressures ranging from 50 Pa to atmospheric pressure. The substrate is commonly heated by electric resistance, inductance or infrared heating. The deposition of coating material takes place atom by atom, on the hot substrate. Although CVD coatings usually exhibit excellent adhesion, the requirements of high substrate temperature limit their applications to substrates which can withstand these high temperatures. CVD process is performed in three different categories, i.e. atmospheric pressure CVD, low-pressure CVD, and ultra-high vacuum CVD, and the last two methods are the most common ones (Mayerson et al., 1992). The low-pressure CVD process permits the deposition of coatings with superior quality and uniformity over a large substrate area at high deposition rates. During the deposition of the coating on the surface of the substrate material the volatile by-products are also produced in certain quantities which are blown away by the gas flow inside the reaction chamber. This process requires a high vacuum and is extensively used in the semiconductors industry providing a solid, high quality, and a high resistance coating

layer on any substrate (Annavarapu et al., 2018; Sojoudi et al., 2017; Nemani et al., 2018; and Sojoudi et al., 2019). The chemical vapor deposition system consists of following modules for the successful running of the system. Gas delivery system, it provides the precursors inside the reaction chamber. Substrate loading mechanism, this is used for introducing the substrates, mandrels etc. Energy source, it helps to generate the sufficient amount of heat to get the precursors react/decompose. Vacuum system, this system is used for the blown away the extra gaseous species which are not participating in the reaction/ deposition. Exhaust system, this system is used for the removal of volatile by-products from the reaction chamber. Process control equipment, it controls the process parameters such as pressure, temperature and time (ASM handbook, Vol. 4, 9th edn.).

Thermal Spraying: The most versatile process of deposition in which the coating material (in the form of rod, wire or powder) is fed to a heating zone where melts and then is propelled to the pre-heated substrate. The "feedstock" material is heated by supplying the required energy through electrical (plasma or arc) or chemical means (combustion flame). The spraying distance from the gun to the substrate material is kept normally in the range of 0.15 to 0.3 m. The molten particles accelerated towards the substrate are cooled to a semi-molten condition. They splatter on the substrate surface and are instantly bonded primarily by mechanical interlocking. Since during the process a substantial amount of heat is transmitted to the substrate material therefore, substrate material is cooled to avoid overheating and distortion. Thermal spraying can provide relatively thick coatings (20 μm to several mm), depending on the process and feedstock, over a large area at high rate of deposition as compared to other coating methods like electroplating, physical and chemical vapor deposition. The coating of flammable substances can also be done because the surface does not heat up significantly. Figure 2.2 shows the schematic diagram of the physical thermomechanical processes that occur

during thermal spraying. The technique has a number of variants such as Flame spraying, Electric arc wire spraying, Plasma spraying and High-Velocity Oxy-Fuel (HVOF) spraying, which are basically different from each other on the basis of the speed of the particles, temperature of the flame and spray atmosphere. Thermal spray technology is exceptionally important for the engineering community, for its (i) high throughput compared to competitive techniques, (ii) significantly improved process control and (iii) lower cost-per-unit mass of applied material, together with overall competitive economics. The thermal spraying technique has following major advantages.

- (a) Various materials such as metals, alloys, ceramics, cermets and carbides can be successfully deposited on any type of substrate material.
- (b) Due to high deposition rate, thick coatings can be successfully deposited.
- (c) Coatings are mechanically bonded to the substrate which also provides a flexibility for the materials which are metallurgically incompatible with the substrate material.
- (d) Parts can be rebuilt very quickly and at a very low cost.
- (e) By using a premium coating material in thermal spray, the parts can outlive in comparison to the original parts.

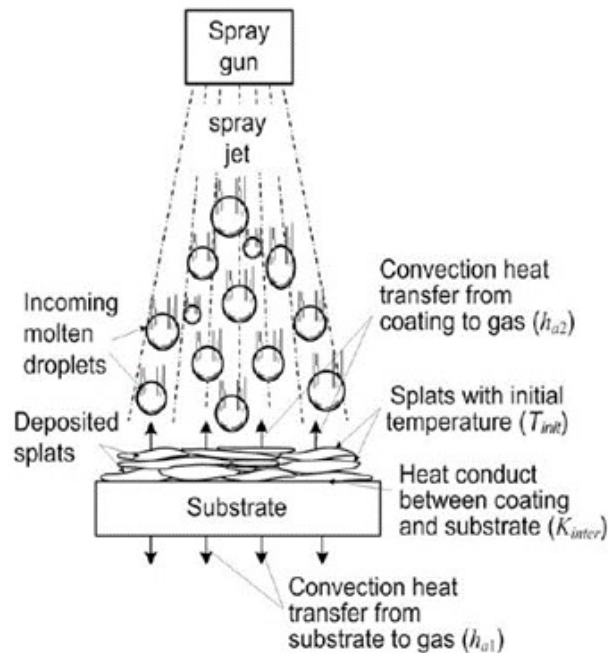


Fig. 2.2 Schematic diagram physical thermo mechanical process during thermal spraying process. (Chen et al., 2010)

Hard Facing: Hard facing, also known as weld overlay, is a family of processes that weld the protective coating to the surface to be protected. Unlike thermal spray processes, hard facing requires that the surface be melted to form a physical, chemical, and metallurgical interface. As a result, hard facing is done on larger components that are not deformed by the heat of application. Furthermore, the interface exhibits a heat-affected zone in which the properties of the surface are altered and also includes regions where the surface material and the applied material are both present. The principal application of hard facing is for the rebuilding of worn components or in the manufacturing of new equipment where large amounts of wear need to be tolerated.

Electroplating: Electroplating, a well-established process with proven benefits in controlling corrosion and wear resistance, is a convenient way of applying coatings of metals with high melting points such as chromium, nickel, copper, silver, gold, platinum,

etc., onto the substrate. The system consists of an electrolytic bath (containing a salt or other compound of the metals to be deposited), two electrodes and a DC power source. When an electrical potential is applied to the electrodes, i.e. one is the material to be coated the other is the donor electrode, the metal is deposited on the substrate by electrochemical dissolution from the donor electrode. The process is conducted under atmospheric conditions and material is deposited with low energy, hence, the coating-substrate adhesion is poor.

2.5 ATMOSPHERIC PLASMA SPRAY

Plasma spraying is the most frequently used thermal spraying technique which finds a lots of industrial applications. Plasma spraying has a unique position due to its flexibility that any type of materials from metallic to nonmetallic can easily be sprayed as coating (Satpathy et al., 2007 and Fauchais et al., 1996). Other key features of plasma spraying are the formation of microstructures with fine, noncolumnar and equiaxed grains, the ability to produce homogeneous coatings that do not change in composition irrespective of the length of deposition time and coating thickness, the ability to process materials in virtually any environment (e.g., air, high pressure, under water). Monolithic and near net shapes can also be produced easily by plasma spraying process. The coatings deposited by plasma spray route have been used as a corrosion, erosion, abrasion, and high temperature wear resistant coatings.

Figure 2.3 shows a schematic diagram of plasma spray process. An arc is created between anode and cathode. The gas molecules undergo ionization in high temperature region which results in the formation of plasma. Generated plasma gas is forced to pass through the annular space between the electrodes. Temperature in the

plasma are very high in the range of 2,000 °C to 20,000 °C which is responsible of melting anything. The ionization is achieved by collisions of electrons of the arc with the neutral molecules of the gas. The plasma protrudes out of the electrode encasement in the form of a flame. To avoid the overheating, electrodes are water cooled. The raw coating material through the hopper in the powdered form is poured into the flame with required feed rate. The powders are found to melt immediately due to gain of energy by plasma and due to momentum provided by primary and secondary gases they move towards the substrate material to form a deposited layer. By this way coating deposition in laminar form commences. Cooling arrangement is required to protect the spray system from excess heating.

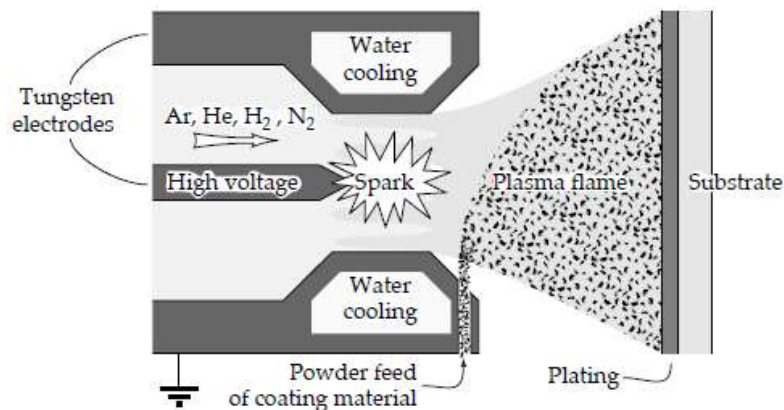


Fig. 2.3 Conventional plasma spray process. (Stachowiak 2nd edition, Engineering Tribology)

2.5.1 MECHANISM OF COATING DEPOSITION

Plasma spray coating is formed when a set of continuous molten particles comes out of the nozzle and strikes on the substrate surface. The microstructure of a particular coating depends on the velocity of the molten particles, temperature of plasma, shape and size of the incident particles. Ideally it is presumed that all the particles which

strike on substrate surface would be completely molten. The particles which do not melt properly might bounce off and thus lower the deposition efficiency. Fabrication of the composite coatings takes place by deposition of the composite powders layer by layer with solidification as the process moves forward and results in the formation of a lamellar microstructure. Ng et al. (2005) have shown that when a liquid droplet strikes the surface at low velocity, it flattens to a disc (shown in Fig. 2.4) which then come to the equilibrium shape of spherical cap to form a cone and then spreads again to the final equilibrium shape determined by the static surface tension forces (shown in Fig. 2.5). At high impact velocities the thin sheet of liquid becomes unstable and disintegrates at the edge into many small droplets leading to splashing.

2.5.2 EFFECT OF DEPOSITION PARAMETER ON COATINGS

The parameters of plasma spraying are interrelated and their cumulative effect actually determines the extent of particle melting, adhesion strength and deposition efficiency of the powder. Deposition efficiency is the ratio of actual amount of powder deposited over the substrate surface and the total amount of powder fed into the gun. A number of parameters have been reported to affect the deposition of coatings (Levingstone et al., 2008). The following sub-sections describe the effect of various parameter on coating deposition.

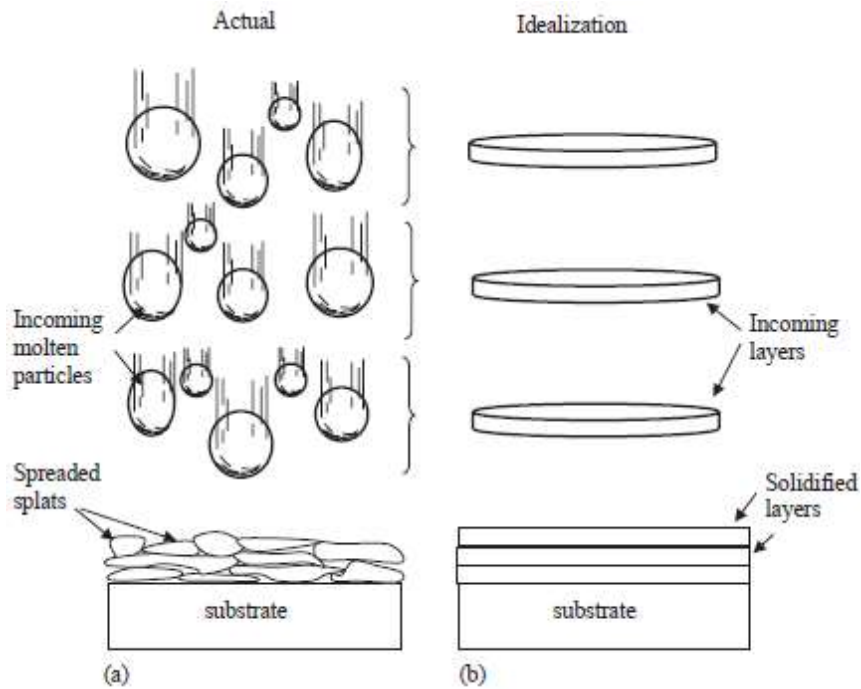


Fig. 2.4 Schematic of the (a) physical plasma spray process and (b) its idealization for modeling. (Ng et al., 2005)

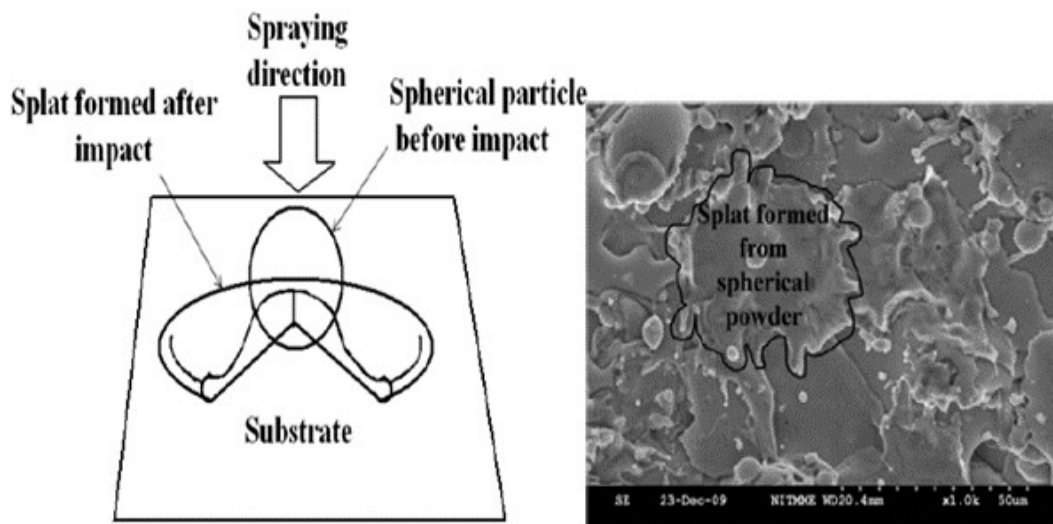


Fig. 2.5 Splat formations after the impact of the spherical powder during spraying. (Behera et al., 2012)

2.5.2.1 Effect of Arc Power

An arc power is electrical power which is supplied to the plasma gas, which in turn gain energy from plasma stream. Arc power actually determines the rate of flow of powder for effective melting with an appropriate contact time. Coddet et al. (1998) have reported that deposition efficiency can be improved with an increase in arc power up to a certain limit, because it increases the particle melting rate. However, further increase of arc power results in a decrease in deposition efficiency due to vaporization of the powder caused by the increased temperature after the complete melting of powder by the optimum arc, because after the complete melting of powder by the optimum arc, the increase in gas temperature causes vaporization of the powdered material.

2.5.2.2 Plasma Gas

The most commonly used gases which are frequently used for plasma generation are argon, nitrogen, helium, hydrogen and air. The selection of a particular plasma gas depends on many factors, such as the design features of the torch, in particular the electrode materials as indicated by Venkatramani (1995). In case of plasma torches employing tungsten cathode, the choice of plasma gas is limited to inert gases and non-oxidizing gases. Gas enthalpy is another important factor deciding the choice of the gas Gerdeman (1972). It has been suggested that argon doped with helium should be used for the small size substrate, because spray cone becomes quite narrow which helps in spraying on small targets. The low cost and high internal energy of nitrogen makes it the most commonly used gas. Argon gas is preferred under the conditions where inert atmosphere is required. Reactive gases like hydrogen, oxygen, chlorine, methane and

ammonia/nitrogen can be used to impart reducing, oxidizing, chloriding, carburizing, or nitriding effects, respectively, to the plasma.

2.5.2.3 Effect of Flow Rate of Carrier Gas

In the plasma spray process primary gas is used as the carrier gas and its flow rate is an important factor in deciding the deposition efficiency. Nash et al. (1961) have pointed out that when the flow rate of the carrier gas is very high then the powders will not be able to face the hottest region of the plasma jet and a very low flow rate will not help to reach the powder successfully into region of plasma jet (as shown in Fig. 2.6). There is an optimum flow rate for each powder which helps in minimizing the (%) fraction of unmelted powder and results in an increase in efficiency.

2.5.2.4 Effect of Mass Flow Rate of Powder

For each powder there is an ideal mass flow rate which has to be determined. The low mass flow rate of the powder keeping all other things constant will be under utilization of the system and coating formation will be slow. On the other hand, at a high flow rate the fraction of un-melted powder particles might increase which, in turn, increases the porosity in the coatings. Nash et al. (1961), and Novak (1988) have reported that due to un-melted powder particles the porosity will increase and efficiency might decrease.

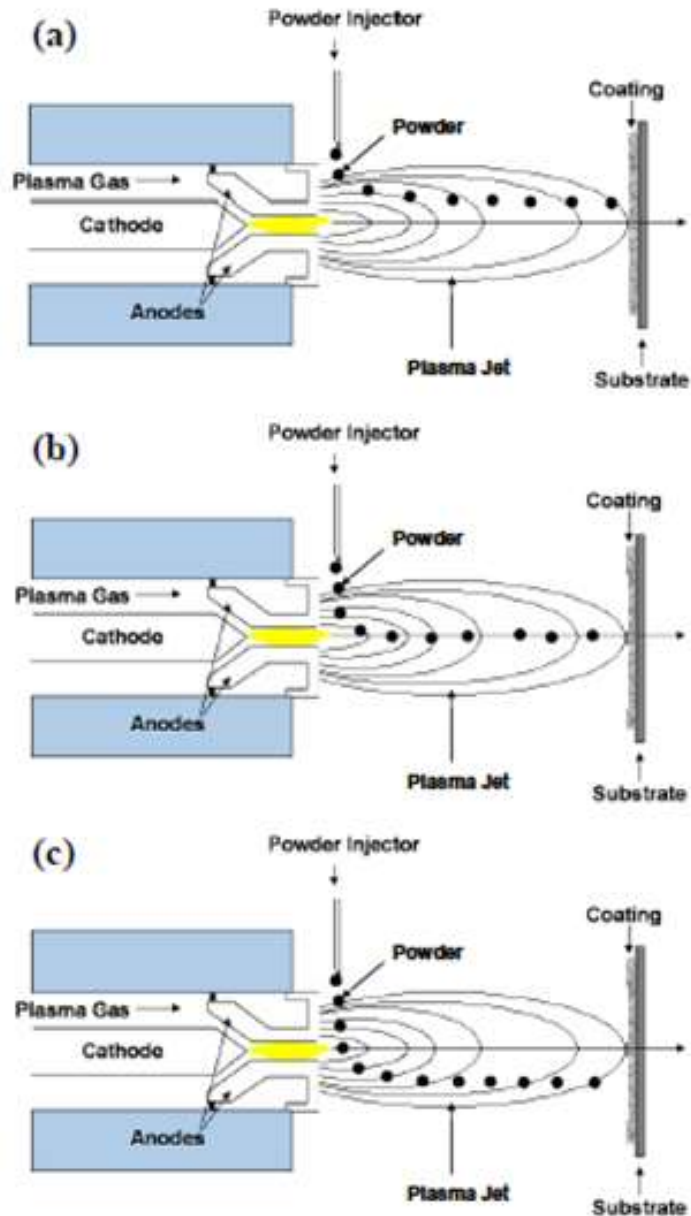


Fig. 2.6 Carrier Gas Flow Rate (a) too low (b) correct (c) too high. (Nash et al., 1961)

2.5.2.5 Effect of Powder Related Variables

The powder variables are powder shape, size, phase composition, size distribution, standard manufacturing processing history etc. These are the very important

parameters which determine the microstructure, porosity of the coatings to an extent. For example, for a given set of parameters, very small size of powder might get vaporized during the spraying process. On the other hand, a large size particles will not melt substantially and will not deposit. Elvers et al. (1990) have reported that the powders which are spherical in size will be different from the angular size powders, hence under the same parameters both powders could not be sprayed.

2.5.2.6 Effect of Stand-Off-Distance (Spray Distance)

The distance between substrate surface and tip of the gun is termed as spray distance. If the spray distance is too long, it might result in freezing of the molten particles before just they reach on the surface of the substrate material. Kang et al. (2006) and Funk et al. (1985) have reported that a short standoff distance does give sufficient time to the particles in flight to melt completely and thus erodes the top of the substrate surface. The large stand-off-distance causes an increase in porosity due to un-melted powder particles and thickness of the coating decreases.

2.6.3.7 Effect of Spraying Angle

The spraying angle affects the adhesive strength of the coating and the splat formation occurs due to the correct spray angle, which is selected on the basis of the nature of the substrate i.e. ductile or brittle. Kang et al. (2005) have reported the splat SEM morphologies of yttria-partially-stabilized (8%) zirconia after impacting droplets on mild steel substrate surface with different angle of (a) 0°, (b) 10°, (c) 20°, (d) 30°, (e) 40°, (f) 50°, (g) 60° are shown in Fig. 2.7.

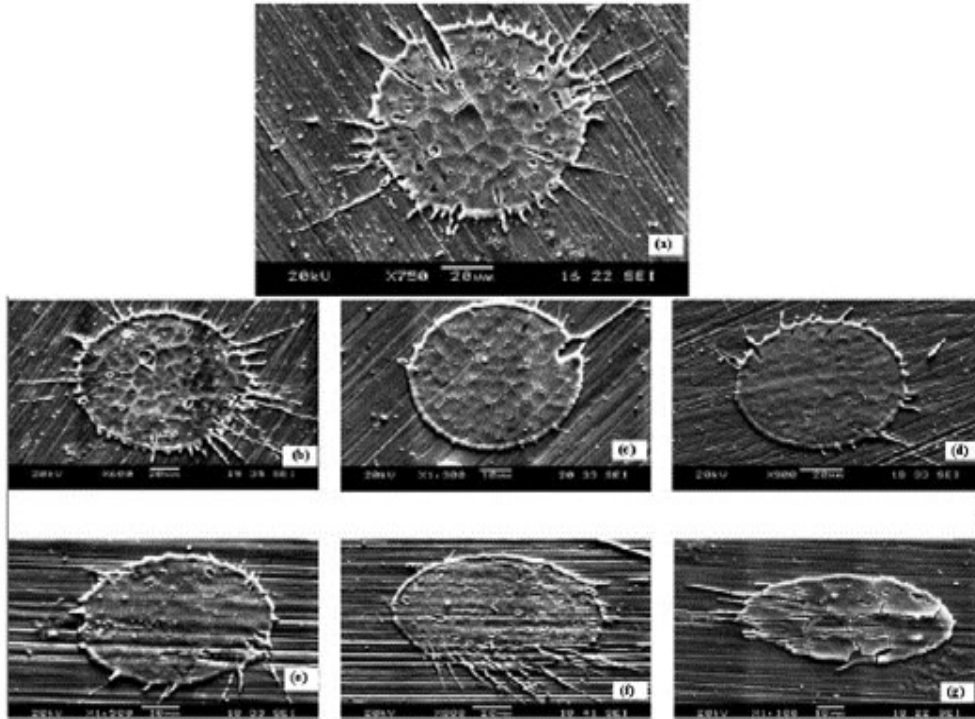


Fig. 2.7 SEM examination of splat morphologies obtained from impacting droplets at substrate inclinations of (a) 0°, (b) 10°, (c) 20°, (d) 30°, (e) 40°, (f) 50°, (g) 60°. (Kang et al., 2005)

2.6 HIGH TEMPERATURE WEAR OF MATERIALS

Due to advancement in the technology, there is an increasing demand, need for mechanical systems that are to work under an extreme range of conditions i.e. high loads, speeds and temperatures. Elevated temperature phenomenon are found in aerospace systems, advanced combustion engines, mining and metal working processes. At elevated temperatures the most alloys and metals show the decreasing trend in the hardness and yield strength. Based on the reduction of the intrinsic mechanical properties, one could assume a lower wear resistance at elevated temperatures. However, this effect should be used with caution since other factors such as microstructural changes, heat conduction, thermal fatigue, material transfer, segregation of elements forming brittle

phases on the substrate or oxidation can alter the tribo-contact region which in turns affect the wear response of the material. A number of studies (Wang et al., 2003; Inman et al., 2006; Roy et al., 2004; Pauschitz et al., 2003; Roy et al., 2002; Radu et al., 2005, 2007; Inman et al., 2005, 2006; and Tu et al., 1998) have been reported on the elevated temperature wear of metallic materials. All the investigations have concluded the formation of a glaze layer on the substrate under certain conditions of load, temperature and sliding speed. Blau (2010) pointed out that at elevated temperature, tribo-layer (glaze layer) is formed at the interface of the two mating parts due to continuous mechanical action. Stott et al. (1973) also highlighted the role of tribo-layers called 'glazes' which generates due to frictional contact at elevated temperature and suggested that glazes (tribo-layer) have the ability to separate out the two mating surfaces in motion and thus avoid the direct contact. Due to continuous sliding glazes can be wear off, but new glazes form and protect the surfaces from further damage. Stott (1998, 2002) have indicated that the oxidized debris also influences the wear behavior at elevated temperatures in different ways. It has been reported that during sliding, some wear debris come out of the interface, have no role on wear behavior whereas some of them get trapped between the mating surfaces. The entrapped wear debris particles experience repetitive deformation and crush to fine particles which then get oxidized. These oxidized particles get collected at some areas and adhere to the mating surfaces resulting in formation of a compacted layer which act as load bearing film and reduces metal-to-metal contact. If the oxide becomes solid before it breaks, a glaze layer is established and the wear usually decreases to very low values. However, it has also been suggested that the presence of oxides at the interface of tribo-systems is not always favorable to reduce the friction and wear. They can act in either a beneficial or detrimental way. For example, the detachment of a hard and brittle oxide may result in an increased wear through abrasive particles, where as a ductile and

lubricious oxide may reduce both friction and wear. The properties of the oxides such as strength, adherence to the substrate, capability to get sintered and thus form glaze layers among others, strongly depend on the materials in contact and the sliding and surrounding conditions. Roy et al. (2004) carried out a systematic study of the elevated temperature wear of 253 MA alloy against 100Cr6 Steel and PM 1000 alloy and reported that formation of different types of layers such as transfer layer (TL), mechanically mixed layer (MML), composite layers (CLs), etc. occurs during high temperature wear processes which play a vital role in governing wear at elevated temperatures.

2.7 SLIDING WEAR OF SOLID LUBRICATING COMPOSITES AND COMPOSITE COATINGS

Wear of metals in air at room temperature in the absence of any lubricant is termed as dry sliding wear. Intensive investigations have been conducted by various investigators to explore different aspects of sliding wear of solid lubricating composites and composite coatings. Researches have mainly been centered on investigating the effects of sliding conditions like load, sliding velocity, temperature, counter face, and solid lubricants which affect the friction and wear of the solid lubricating composites and composite coatings. Extensive review of literature has been carried out on solid lubricating composites and composite coatings involving solid lubricants and fabricated by different fabrication techniques. Some of them are presented below depending on the factors which predominantly affect the friction and wear of coatings and composites.

Li et al. (2020) investigated the tribological properties of nanostructured NiCrAlY-Mo-Ag composite coating deposited via Plasma spray on Inconel 718 against Al₂O₃ ball using a ball-on-disk high-temperature tribometer at a load of 10 N and a speed of 0.3 m/s at room temperature (RT), 300, 500, 700 and 900 °C and reported a

continuously decreasing trend of both the coefficient of friction and wear rate with increasing temperature from RT to 900 °C. It has been concluded that silver provided the effective lubrication in the low temperature regime below 400 °C, whereas at elevated temperatures, the formation of glaze layers of silver and nickel molybdates resulted in reduced friction and wear.

Zhang et al. (2017) investigated the friction and wear behavior of plasma sprayed NiCoCrAlY-Cr₂O₃-AgMo coatings at a fixed temperature of 500 °C under different normal loads of 1, 5 and 10 N and observed a decrease in friction coefficient and wear rate with increasing load with a minimum value of friction coefficient (~ 0.3) at 10 N. The observed behavior has been attributed to the formation of a lubricating film of Ag₂MoO₄ at the interface.

Li et al. (2017) also studied the tribological behavior of plasma sprayed NiCrAlY-Mo-Ag composite coating against Si₃N₄ ball under RT, 300, 500, 700 °C and 900 °C using a ball on disc high-temperature tribometer at 10 N and 0.3 m/s and observed a decrease in both the coefficient of friction and the wear rate from RT to 300 °C which was followed by an increase up to 500 °C and a continuous decrease until 900 °C. Silver has been suggested to provide required lubricity in low temperature regime (< 400 °C). However, the favorable lubricity at temperatures beyond 500 °C has been attributed to the formation and presence of glazed layers of NiO and silver molybdates at the worn surface.

Wang et al. (2017) examined the tribological behavior of NiCrAlY based composite coating containing Ag-MoO₃ prepared through high energy ball milling and laser cladding using a ball-on-disk tribometer against Si₃N₄ ceramic ball at a load of 3 N and a constant speed of 360 rpm under different temperatures of RT, 200, 400, 600,

and 800 °C. The authors reported a decreasing trend of coefficient of friction and wear rate in low temperature regime RT-200 °C, followed by an increase from 200-400 °C and a decrease thereafter till 800 °C. The observed behavior has been attributed to the lubrication rendered by silver till 200 °C and the loss of effectiveness of silver between 200 to 400 °C. However, a decrease beyond 400 °C has been ascribed to the generation of Ag_2MoO_4 lubricating phase (glaze layers).

Xin et al. (2017) investigated the tribological behavior of $\text{NiCrAlY/Cr}_3\text{C}_2(\text{NiCr})/\text{Cu}/\text{MoO}_3$ self-lubricating composite coating deposited through laser cladding on GH4169 alloy by carrying out tests at 25, 200, 400, 600, and 800 °C under a load of 3N and a speed of 0.19 m/s against Si_3N_4 ceramic ball using a ball-on-disk tribometer. The coefficient of friction and wear rate have been reported to increase with increasing temperature RT-200 °C, followed by a continuous decrease until 800 °C. The favorable lubricity at elevated temperature has been attributed to formation of CuMoO_4 and other lubricious oxides such as MoO_3 , Cr_2O_3 , CuO and NiO . In another study, Xin et al. (2016) studied the friction and wear behavior of laser cladded $\text{NiCrAlY/Cr}_3\text{C}_2(\text{NiCr})/\text{V}_2\text{O}_5/\text{Ag}_2\text{O}$ coating under RT, 200, 400, 600, and 800 °C against Si_3N_4 ceramic ball and found that the coefficient of friction first increased with increasing temperature from RT-200 °C and decreased thereafter till 800 °C. The authors reported an increase in wear rate in low temperature regime from RT-400 °C and a decrease beyond that until 800 °C. The observed behavior has been attributed to the formation of Ag_3VO_4 and AgVO_3 lubricating layers on the worn surface.

Li et al. (2017) explored the friction and wear characteristics of plasma sprayed NiAl-Ag-Mo composite coating deposited on Inconel 718 under RT, 300, 500, 700 and 900 °C using a ball-on-disk high-temperature tribometer against Al_2O_3 ceramic

ball at a load of 10 N, speed 0.3 m/s, before and after heat treating the coating at 400, 500 and 600 °C and reported a continuous decrease in coefficient of friction with increasing temperature from RT to 900 °C. However, the wear rate of the coating has been shown to follow decreasing trend from RT to 300 °C, followed by an increases up to 500 °C and a decrease beyond that till 900 °C. Authors have attributed the observed behavior to the effectiveness of silver in providing lubrication in the low temperature regime and the formation of silver and nickel molybdates lubricating films at elevated temperatures.

Chen et al. (2014) investigated the tribological properties of NiMoAl–Cr₃C₂–Ag composite coatings deposited by high velocity oxy-fuel (HVOF) spray on stainless steel disks by carrying out tests against a Si₃N₄ ball at different temperatures i.e. 20, 200, 400, 600 and 800 °C at a constant load of 15 N and speed of 600 r/min using a ball-on-disk tribometer. Coatings have been reported to maintain a low coefficients of friction ~ 0.3 and wear rate of the order of 10⁻⁶ mm³/Nm at all the temperatures except 400 °C. The observed behavior has been attributed to the presence of silver which provided effective lubrication below 400 °C and silver molybdates formed due to tribo-chemical reactions which acted as high temperature lubricants. Further, the authors also conducted tests at four different loads of 3, 7, 11 and 15 N and at a fixed speed and temperature of 600 r/min and 400 °C, respectively, and reported an increasing trend of coefficient of friction and wear rate with increasing trend.

In another study, Chen et al. (2014) investigated the high temperature tribological behavior of an adaptive NiMoAl-Ag composite coating (HVOF) under 20, 200, 400, 600, and 800 °C using a ball-on-disk high-temperature tribometer against Si₃N₄ ceramic ball under the load of 5N, speed of 0.1 m/s and observed a decrease in coefficient of friction from RT to 200 °C, followed by an increase up to 400 °C and then

a decrease until 800 °C. The wear rate has been reported to increase from RT-400 °C followed by a decrease until 800 °C. The observed behavior has again been ascribed to the lubricious nature of silver till 400 °C and formation of glaze layers of silver and nickel molybdates at elevated temperatures.

Chen et al. (2013) examined the tribological performance of plasma sprayed NiCrAlY-Ag-Mo composite coating deposited on stainless steel using a high temperature tribometer at a load of 5 N, sliding velocity of 0.3 m/s, under RT, 200, 400, 600 and 800 °C and reported that NiCrAlY-Ag-Mo composite coating had a low coefficient of friction (~ 0.3) and wear rate of the order of 10^{-5} mm³/Nm at all testing temperatures. The coefficient of friction and wear have been found to show an increasing trend in a low temperature regime from RT- 400 °C, whereas, these have been observed to decrease beyond 400 °C and the behavior has been attributed to the favorable lubrication of Silver in low temperature regime (RT-400 °C) and presence of silver molybdates and molybdenum oxide at higher temperatures.

Niu et al. (2012) investigated the tribological properties of Ni₃Al-Ag-Mo-BaF₂/CaF₂ self-lubricating composite coating prepared through powder metallurgical process, under RT, 200, 400, 600, 800 °C and 1000 °C using a ball-on-disk high-temperature tribometer against Si₃N₄ ceramic ball at a load and speed of, 20 N and 0.2 m/s, respectively. The coefficient of friction of the coating showed an increasing trend from RT to 600 °C followed by a decreases till 1000 °C, whereas the wear rate increased from RT to 200 °C, and decreased thereafter until 1000 °C. It has been concluded that silver provided efficient lubrication in low temperature regime (below 400 °C) whereas at elevated temperatures BaF₂/CaF₂ and the glaze layers (tribo-layers), formed by the oxidation of fluorides performed as effective lubricants.

Du et al. (2011) investigated the tribological performance of NiCr/Cr₃C₂-NiCr/hBN coatings under RT, 300, 500, 600 and 800 °C using ball-on-disk configuration against Si₃N₄ ceramic ball at a load of 9.8 N and sliding velocity of 0.188 m/s and reported a decrease in coefficient of friction right from RT to 800 °C. It has been concluded that layered h-BN reduces the real area of contact between two mating pairs and also prevents the severe adhesion which helps in reducing the coefficient of friction.

Du et al. (2010) synthesized plasma sprayed Ni₃Al-hBN composite coatings containing different amounts (5, 10, 15 and 20 wt. %) of hBN and investigated their room temperature tribological behavior against Si₃N₄ ball at a load of 4.9 N and speed of 0.188 m/s by conducting tests on a ball on disk tribometer. The coefficient of friction has been reported to decrease with increasing wt. % of hBN in the coatings, whereas the weight loss has been shown to decrease from 0 to 5 wt. %, followed by an increase up to 15 wt. % and a decrease thereafter until 20 wt. % of hBN addition in the coatings. It has been concluded that hBN offers favorable lubricity if the addition is less than 10 wt. %.

Huang et al. (2009) investigated the tribological properties of NiCr/Cr₃C₂-BaF₂.CaF₂ composite coating (plasma spray) under RT, 300, 500, 650, and 800 °C using a ball-on-disk high-temperature tribometer against Si₃N₄ ceramic ball at a load of 9.8 N and a speed of 0.188 m/s. The authors observed that the coefficient of friction of the coating decreased from RT to 500 °C followed by an increase at 650 °C and a decrease beyond that. The wear rate of the coating increased from RT to 300 °C and decreased thereafter up to 650 °C before increasing slightly until 800 °C. The formation of low shear strength tribo-layers and the transfer layers on the counter ball have been reported to be responsible for the low friction and wear at elevated temperatures.

Zhang et al. (2009) investigated the tribological behavior of Ni₃Al–hBN–Ag composite coating deposited on Ni-based super alloy, under RT, 200, 400, 600, and 800 °C using a ball on disc high-temperature tribometer against Si₃N₄ ball at a load of 5 N and a speed of 0.132 m/s. The coefficient of friction decreased from RT to 200 °C and increased thereafter up to 400 °C before decreasing again till 800 °C. The wear rate decreased from RT to 200 °C and increased thereafter up to 600 °C before decreasing again for 800 °C. The reported values of coefficients of friction are in the range of 0.32–0.48 and the wear rates $(2.3–5.2) \times 10^{-5} \text{mm}^3/\text{Nm}$ from RT to 800 °C. The composite coating has been reported to provide self-lubricating properties right from RT to 800 °C due to a synergetic lubricating action of Ag and hBN.

Zhen et al. (2016) studied the tribological characteristics of nickel-alloy based self-lubricating composite (82.5% nickel-alloy-12.5% Ag–5% BaF₂/CaF₂) against Si₃N₄ ball at the load of 5N under different temperatures (RT, 200, 400, 600 and 800 °C) and speeds (0.2, 0.4, 0.6, 0.8 and 1.0 m/s). The coefficient of friction has been reported to decrease from RT to 400 °C followed by an increase up to 600 °C and a decrease until 800 °C at all sliding speeds and testing temperatures, whereas the wear rate has been found to increase from RT to 600 °C followed by a decrease until 800 °C at all sliding speeds. It has been concluded that the composite provides satisfactory lubricity in a range of temperature from RT to 800 °C due to the formation of glaze layers at elevated temperatures.

Liu et al. (2014) studied the tribological behavior of self-lubricating NiAl/Mo–AgVO₃ composites under RT, 300, 500, 700 °C and 900 °C using pin-on-disc high temperature tribometer against Inconel as a counterpart material at a linear velocity of 0.287 m/s and a load of 2 N and reported a continuously decreasing trend of coefficient

of friction with increasing temperature from RT to 900 °C. However, the wear rate of the composites showed a decreasing trend from RT to 300 °C followed by an increase up to 500 °C and a decrease thereafter until 900 °C. The observed behavior has been attributed to synergistic lubricating action of metallic Mo and AgVO₃ lubricants.

Feng et al. (2017) investigated the tribological behavior of NiAl–NbC–Ag composite fabricated by mechanical alloying and vacuum-hot-pressing sintering by carrying out tests at RT, 300, 700 and 900 °C at a load of 20 N under speed of 0.105 m/s on a ball-on-disc high-temperature tribometer against Al₂O₃ ball. The friction coefficient and wear rate have been reported to follow a decreasing trend for NiAl–3NbC–10Ag composite up to 500 °C followed by an increase up to 700 °C and a decrease thereafter till 900 °C. The behavior has been explained on the basis of the formation and presence of lubricous glazed layers.

Zhu et al. (2011) examined the tribological behavior of NiAl–Cr–Mo–CaF₂ (P/M) composite at different temperatures (20, 200, 400, 600, 800, and 1000 °C) at a sliding speed and normal load of 0.188 m/s and 10 N, respectively, against Si₃N₄ ball using a ball-on-disc tribometer. The friction and wear have been reported to increase with increasing temperature from RT to 400 °C followed by a continuous decrease up to 1000 °C. Also, the composite had been reported to possess a favorable friction coefficient ~ 0.2 and an excellent wear resistance of about $1 \times 10^{-5} \text{ mm}^3\text{N}^{-1}\text{m}^{-1}$ at the high temperatures (800 and 1000 °C). The authors attributed the favorable lubricity to the formation of glaze film on the worn surface consisting mainly of CaCrO₄ and CaMoO₄ which acted as high-temperature solid lubricants. In another study, the same authors, Zhu et al. (2015) investigated the tribological behavior of self-lubricating NiAl–Cr–Mo–CaF₂–Ag composite by conducting tests at different temperatures of RT, 200,

400, 600, 800, and 1000 °C at a sliding speed of 0.2 m/s and the load of 10 N against a Si₃N₄ ball and reported the similar trend of variation of friction and wear with temperature as observed for NiAl–Cr–Mo–CaF₂.

Zhai et al. (2015) investigated the tribological behavior of Ni₃Al-WS₂-Ti₃SiC₂ composites at RT, 200, 400, 600 °C, and 800 °C using a ball on disc high temperature tribometer against Si₃N₄ ball by conducting tests at a normal load of 10 N and a speed of 0.2 m/s and reported low coefficients of friction (0.18–0.39) and wear rates ($1.5\text{--}3.7 \times 10^{-5} \text{ mm}^3\text{N}^{-1}\text{m}^{-1}$). In low temperature regime i.e. below 400 °C whereas the glaze layer was formed on the worn surface of composites during the sliding process, provided effective lubrication at elevated temperatures.

Zhu et al. (2012) studied the tribological behavior of Ni₃Al–Ag–BaF₂/CaF₂–W composites (P/M) under 200, 400, 600 °C and 800 °C using ball-on-disk high-temperature tribometer against Si₃N₄ ceramic ball at a load of 10 N and a speed of 0.19 m/s and obtained low coefficients of friction and wear rates which showed an increasing trend of variation with increasing temperature from RT to 600 °C followed by a decrease for 800 °C. The low coefficients of friction and wear rates over a broad temperature range have been attributed to the occurrence of a synergistic action among Ag, BaF₂/CaF₂, BaWO₄, and CaWO₄.

Liu et al. (2012) investigated the tribological properties of adaptive Ni-based composites with addition of 10 and 20 wt. % Ag₂MoO₄ under RT, 300, 500 °C and 700 °C using a pin-on-disk high-temperature tribometer against Inconel 718 alloys disk at a load of 2 N and a speed of 0.287 m/s. The coefficient of friction and wear rate of the composites have been reported to decrease with increasing temperature right from RT to 700 °C and increasing Ag₂MoO₄ contents and the composites with addition of 20 wt.%

Ag_2MoO_4 exhibited the lowest coefficient of friction (0.26) and wear rate ($1.02 \times 10^{-5} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$) at 700°C . The favorable lubricity at elevated temperature has been attributed to synergistic behavior of silver molybdates and Fe oxide (transferred from the disk material to the pin) formed on the worn surface.

Shi et al. (2014) investigated the tribological performance of Ni_3Al matrix composites (NMSC) prepared via spark plasma sintering and containing varied amounts of WS_2 (W), Ag (A) and hBN (h) (0, 10, 15, 20 wt. % WAh) and a fixed 5 wt. % of TiC under RT, 200, 400, 600, and 800°C using a ball on disc high-temperature tribometer against Si_3N_4 ball at a load of 10 N and a speed of 0.234 m/s and reported that coefficient of friction as well as wear rate of the composites decreased from RT to 600°C followed by an increase until 800°C . The favorable lubricity has been reported for (NMSC with 15 wt. % WAh, 5 wt. % TiC) in a range of temperatures from RT to 800°C and the same has been attributed to synergetic action of a combination of lubricants WAh with the reinforced phase of TiC.

Zhu et al. (2015) studied the tribological behavior of Ni_3Al matrix composites containing silver and barium salt (BaCrO_4 , BaMoO_4) under 20, 400, 600°C , and 800°C using a ball on disc high-temperature tribometer against Si_3N_4 ball at a load of 20 N and a speed of 0.19 m/s and indicated a decreasing trend of friction coefficient from RT to 400°C followed by a decrease until 800°C . However, the wear rate of the composites increased from RT to 400°C and decreased thereafter till 600°C followed by an increase until 800°C . The favorable lubricity in a broad range of temperature has been attributed to the synergistic effect of Ag with barium salts.

Shi et al. (2014) investigated the tribological behavior of NiAl based self-lubricating composites containing different solid lubricants (PbO , Ti_3SiC_2 – MoS_2 ,

Ti₃SiC₂-WS₂) under RT, 200, 400, 600 °C and 800 °C using a ball on disc high-temperature tribometer against Si₃N₄ ball at a load of 10 N and a speed 0.2 m/s. The coefficient of friction of the composites has been reported to show a decreasing trend from RT to 400 °C followed by an increase up to 600 °C and a decreases thereafter until 800 °C, whereas the wear rate of the composites has been shown to present an increasing trend from RT to 200 °C followed by a decrease up to 400 °C and an increase up to 600 °C and a decrease again until 800 °C. The favorable lubricity has been reported by the composites containing Ti₃SiC₂-MoS₂ solid lubricant combination in NiAl matrix over a wide range of temperatures with MoS₂ providing an effective lubrication in low temperature regime (< 400 °C), and a synergetic lubricating effect of Ti₃SiC₂-MoS₂ binary lubricant providing the same at elevated temperatures.

Liu et al. (2013) studied the tribological properties of Ni-based composites (P/M) containing Ag and MoS₂ under RT, 500 °C, and 700 °C using a pin on disc high-temperature tribometer against Inconel 718 disks at a load of 2 N and a speed 0.287 m/s and reported a decreasing trend for both coefficient of friction as well as wear rate from RT to 700 °C. The observed behavior has been attributed to the formation of silver molybdates at elevated temperatures and their presence at the mating pairs.

2.8 FORMULATION OF THE PROBLEM

A critical review of literature presented above indicates that several studies have been carried out on the synthesis of coatings deposited through different techniques or composites prepared by different routes containing a combination of solid lubricants and evaluation of their tribological performance under various conditions of load, speed, temperatures and against different counterface materials. A number of researches have

also examined the possibility of a synergistic action among a combination of solid lubricants (Ag, MoS₂, CaF₂/BaF₂, hBN etc.) in providing the effective lubrication from room temperature to elevated temperatures (800 to 1000 °C). However, to the best of our knowledge there is no study reported on the high temperature friction and wear behaviour of atmospheric plasma spray deposited Ni based coatings containing a combination of Ag, MoS₂ and Hexagonal Boron Nitride (hBN) as solid lubricants. Hexagonal Boron Nitride (hBN) has been indicated to be a clean lubricant which is thermally stable up to 900°C and therefore, could be a promising lubricant for high temperature applications. A few studies have also reported a reduction in both friction and wear of Ni based composites or coatings by incorporation of hBN as a solid lubricant. However, the potential of hBN as a high temperature solid lubricant is yet to be fully exploited. Hence, it becomes imperative to conduct a detailed investigation on the evaluation of the potential of hBN as a solid lubricant in conjunction with Ag and MoS₂ in Ni based coatings under different loads, speeds and temperatures ranging from room temperature (RT) to 800 °C.

The present study is motivated by the need to increase the life time of the advanced technological systems which are to work under high temperatures by developing coatings that are able to provide self-lubricating properties in the extended regime of temperature right from room to elevated temperatures. Hence, the present investigation aims to deposit NiAl based coatings containing Ag, MoS₂ and hBN as solid lubricants via atmospheric plasma spray and to evaluate their tribological performance by carrying out sliding wear tests from RT to 800 °C, at different loads and speeds. The study also intends to explore the effect of the varying addition of hBN on friction and wear characteristics of these coating as well as occurrence of any synergetic action of hBN in conjunction with Ag and MoS₂ in extending the regime of lubrication and to establish the operative mechanisms of wear under the conditions used in the investigation.