Review of Tribology (Friction, Wear & Lubrication) study on Titanium and its Alloy surfaces

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Abstract: Titanium alloys are most effectively used in corrosion resistant material application in the different industries like chemical industry, biomedical industry etc and also has been very useful in Micro Electro Mechanical System for its mechanical and physical properties. So improvement of tribological properties of titanium and its alloy is necessary. Several authors were tried to improve tribological properties by surface modification and coating. These coatings are organic and inorganic according to the applications. Some coatings have been shown low coefficient of friction and high durability limits of wear for their usage in some applications.

INTRODUCTION:

Tribology is the knowledge and engineering of interacting surfaces in relative motion. The word “Tribology” originates from the Greek word “Tribos” meaning “rubbing” or to rub and suffix “Ology” means “the study of”. Therefore, Tribology is “the study of rubbing or “the study of things that rub” [1]. It includes the study and application of the principles of friction, wear, lubrication and surface modification.

Friction: The force resisting the relative motion of solid surfaces, fluid layers, and/or material elements sliding against each other is known as friction. The different types of friction are as: When relative lateral motion of two solid surfaces in contact resists is known as Dry Friction. It’s subdivided into static friction between non-moving surfaces, and kinetic friction between moving surfaces. When the friction between layers with in a viscous fluid that are moving relative to each other known as Fluid Friction. Lubricated friction is a case of fluid friction where a fluid separates two solid surfaces and Skin friction is a component of drag, the force resisting the motion of a solid body through a fluid.

Wear: It’s continuous loss due of surface material to rubbing action. It’s related to interactions between surfaces and more specifically the removal and deformation of material on a surface as a result of mechanical action of the opposite surface. The need for relative motion between two surfaces and initial mechanical contact between asperities is an important distinction between mechanical wear compared to other processes with similar outcomes. Wear are different types which are Adhesion Wear, Abrasive Wear, Surface fatigue, Fretting Wear and Erosive Wear.

Lubrication: For lubrication property study, the "Stribeck curve" or "Stribeck–Hersey curve" (named after Richard Stribeck and Mayo D. Hersey) (shown in figure 1) was developed in the first half of the 20th century which is used to categorize the friction properties between two surfaces. The research of Professor Richard Stribeck (1861–1950) was performed in Berlin at the Royal Prussian Technical Testing Institute (MPA, now BAM). Stribeck curves are demonstrating the variation in friction as a function of either relative speed or viscosity or contact load [2]. Similar work was earlier performed around 1885 by Prof. Adolf Martens (1850–1914) at the same Institute and in the mid 1870s by Dr. Robert H. Thurston [3] at the Stevens Institute of Technology in the U.S. Prof. Dr. Thurston was therefore close to establishing the Stribeck curve, but he presented no Stribeck-like graphs, as he obviously did not fully trust in the relevance of this dependency. Since that time the Stribeck curve has been a classic reference curve describing friction phenomenon.

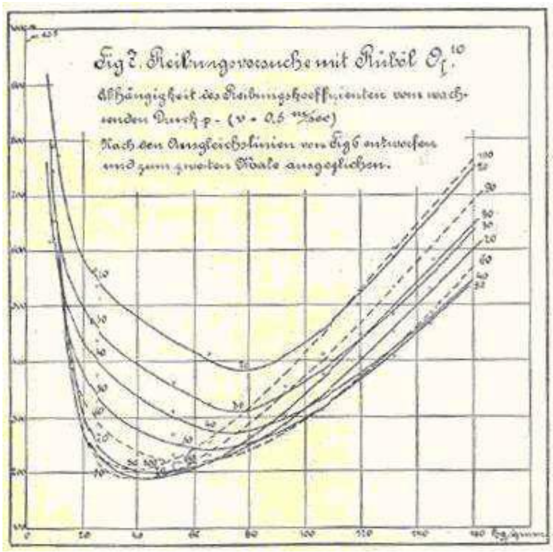

Fig. 1: Typical Stribeck curves obtained by Martens [http://en.wikipedia.org/wiki/File:Martens_curves.JPG]

The systematically studied the variation of friction between two liquid lubricated surfaces by Stribeck. His results were presented on 5 December 1901 during a public session of the railway society and published on 6 September 1902. They clearly showed the minimum value of friction as the discrimination between full fluid-film lubrication and some solid asperity interactions. Stribeck studied different bearing materials and aspect ratios D/L from 1:1 to 1:2. The maximum sliding speed was 4 m/s and the geometrical contact pressure was limited to 5 MPa. (These operating conditions were related to railway wagon journal bearings).

Friction regimes for sliding lubricated surfaces have been broadly classified into

- Solid/boundary friction
- Fluid friction
- Mixed friction or Elasto Hydrodynamic friction

Stribeck curves show a minimum in friction as the demarcation between full fluid-film lubrication and the region with asperity interactions.

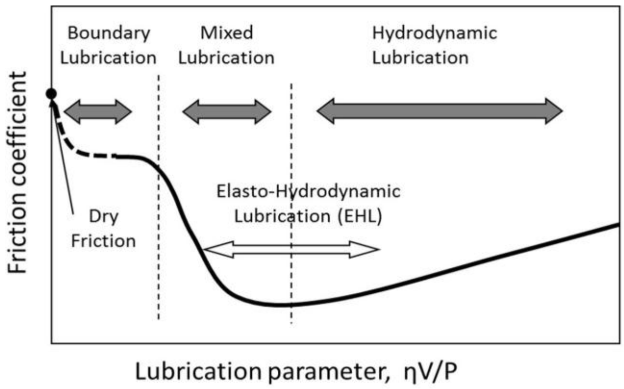

Fig.2: Stribeck curve [4]

Boundary lubrication is defined as a condition of lubrication of metals in which the friction and wear between two surfaces in relative motion which are determine by the properties of the surfaces. Metal to metal contact occurs and the chemistry of the system is involved. Physically absorbed or chemically reacted soft solid films support contact loads usually these solid films are very thin. The boundary lubrication regime plays a very important role in determining the life span of any of the two mating parts under liquid-lubricated conditions. It is during the start\stop cycles when insufficient fluid is available to fully separate the surfaces in relative motion and thus unusual wear takes place; a case of boundary lubrication. Many animal and vegetable fats and oils possess the properties of effective boundary lubrication. From industrial point of view, the most important are:

- Stearic acid (lard oil and mutton tallow).
- Palmitic acid (cotton seed oil).
- Palm oil
- Oleric acid (olive oil)

The efficiency of even the best boundary lubricants decreases when the temperature increases and when they are desorbed (reverse process of adsorption) the friction and wear are almost as high as in the absence of lubrication. Besides, at very high temperatures (≈ 250^{o}C and above) the oxidation of the lubricant may occur and produce injurious products. Hence, for the surfaces which operate under very harsh conditions, more stable protective films are required, which are provided by EP Lubricants.

Lubricants are agents introduced between two surfaces in relative motion to minimize friction. Selection and application of lubricants are determined by the functions they are expected to perform. The principal functions of lubricants are to:

- control friction
- control wear
- control temperature
- control corrosion
- remove contaminants
- form a seal (grease)

In the lubrication base oil/additives plays a very important role. They will be prone to contamination and decomposition in the exacting working conditions. Hence certain chemical compounds and other agents which are termed as additives are added to the oil. Most modern lubricant additives can be classified as follows:

- Those designed to protect the lubricant in service by maintaining deterioration.
- Those that protect the lubricant from harmful fuel combustion products.
- Those which improve existing physical properties or impart new characteristics.

Extreme pressure lubricants are a class of lubricants to which certain active chemicals or chemical groups have been added. These additions are called EP additives and generally are:

- Chlorine (chlorinated esters etc).
- Sulphur (Sulphurised fats and oils etc).
- Phosphorus (tricresyl Phosphate etc).

Additives must have the following properties:

- Solubility in base petroleum oil
- Insolubility in and lack of reaction with aqueous solution.
- Should not impart dark colour to the oil
- Low volatility
- Additives must be stable in blending, storage and use.
- Additives should not impart unfavorable odour.

Application of Tribology:

Tribology is used in every field of engineering such as industries (Biomedical, chemical & production etc), microelectro mechanical or nanoelectro mechanical systems (MEMS/NEMS). This area has grown tremendously by continuous research of Tribology scientist. Titanium and its alloys are most effectively used in corrosion resistant material application in the different industries like chemical industry, biomedical industry etc and also has been very useful in Micro Electro Mechanical System for its mechanical and physical properties. In MEMS/NEMS applications, lubrication is required to reduce adhesion, friction and wear to make sure the reliability and strength of devices. [5].

Titanium and its alloys:

William Gregor was discovered titanium metal in 1791. Martin Klaporth, a Berlin chemist, independently isolated titanium oxide in 1795. He named it titanium after Greek mythological name “Titans”. The most popular titanium alloy Ti6Al4V was developed in the late 1940s in the United States [6]**.** The ASTM defines a number of alloy standards from Grade 1 to 38 (ASTM B861 - 10 Standard Specifications for Titanium and Titanium Alloy Seamless Pipe). Ti6Al4V is the most commonly used titanium alloy for biomedical and industrial applications. Its chemical composition consists of 6% aluminum, 4% vanadium, 0.25% (approximate) iron, 0.2% (approximate) oxygen and remaining of titanium. It is significantly stronger than pure titanium while stiffness and thermal properties are same as that of pure titanium (although thermal conductivity is about 60% lower in Grade 5 Ti compared to that of pure Ti). Ti6Al4V is most widely used among titanium alloys [7] and is considered as the "workhorse" of the titanium industry.

Application of titanium and its alloys in many areas is limited by its property of tribology such as high coefficient of friction, poor wear durability and low surface hardness. Its poor tribological properties are caused by severe adhesive wear with a strong tendency to seizure, low abrasion resistance and the lack of mechanical stability of the oxide layer [8]. Tribology of titanium and its alloy have found great interest among researchers due to possible application of titanium alloys with improved tribological properties in many potential areas. In industrial applications, various surface treatments such as thermo-chemical processes, energy beam surface alloying treatments have been proposed by scientist to address the tribological limitations of titanium alloys [9]. Plasma nitriding and bio-ceramic coatings are widely investigated solutions to improve the tribological properties of alloys in orthopedic implants for biomedical applications. [10]. the research methodology generally used by different researchers is

1. Substrate (Polishing or Grinding)
2. Cleaning and pretreatment
3. Coating deposition
4. Characterization of Coating (SEM, XRD etc is used)
5. Investigation of friction and wear mechanisms

Methods used for improving the tribology properties of Titanium and its alloy:

For improving the properties of titanium and its alloy we have done surface treatments (thermal spray coatings, electroplating, physical vapor deposited coating and surface modifications) & thermo chemical processes etc. [9]. Due to the operational difficulty and its higher cost of PVD and CVD coating techniques, polymer coatings is used as a good alternative protecting technology [11]. Thin film coatings of polymer have also become popular in tribology due to their effectiveness and potential applications [12]. Thin film coating method can be applied to improve tribological performance of materials by applying a thin layer of a low friction coefficient and wear resistant material. Commonly used polymers for coatings are polytetrafluoroethylene (PTFE), polyetheretherketone (PEEK), ultra high molecular weight polyethylene (UHMWPE), epoxy, polydimethylsiloxane (PDMS), self assembled monolayer and polymethylmethacrylate (PMMA).

PTFE coating is used in tribological applications for its excellent properties like low friction coefficient, high chemical resistance and high temperature stability. It has poor wear and abrasion resistance which lead to failure in the machine parts [13].

PEEK is also a suitable polymer for coating for its excellent chemical resistance, tribological properties and high strength.

UHMWPE is another coating material which is linear homo-polymer and the degree of polymerization is up to 200,000. It is a unique polymer with excellent impact resistance, abrasion resistance, chemical inertness and lubricity. This can have average molecular weight of up to 6 million g/mol. This polymer has outstanding physical and mechanical properties. For its excellent wear resistance, this coating has the potential to provide a solution for tribological limitations of titanium alloys in biomedical and industrial applications.

Another method of coating is Ultra-thin organic molecular layers which have also found application as the lubricants for MEMS systems [14-16]. There are first and foremost two methods to form lubricant layers; Langmuir–Blodgett method and Self-assembly method [17]. Langmuir–Blodgett (L-B) method can’t be applied for three dimensional surfaces. It’s used mainly for flat surfaces for example magnetic recording media [18; 14] and also L-B films have only physically bonding with the substrate by Vander Waals forces [19]. Compared to L-B, self-assembled monolayer’s (SAMs) have easy preparation methods and possess greater properties for example low thickness, physical properties and chemical properties and these monolayer have good covalent bonding with the substrate. It also change the length of molecule and also have the cross linking properties within the layer. These properties make SAMs more attractive than the L–B films [17]. SAMs are ordered molecular assemblies formed spontaneously by the immersion of a substrate into a solution of the active surfactant due to adsorption of the surfactant with affinity of its head group to substrate [17]. Molecular structure and cross-linking of SAMs also affect the friction and wear properties of coatings.

It has different terminal groups which makes the film surface hydrophilic or hydrophobic. For a hydrophobic surface A non-polar methyl (-CH_3) or trifluoromethyl (-CF_3) terminal group are used which have low surface energy. The surface terminal groups such as alcohol (-OH) or carboxylic acid (-COOH) groups are used for achieve a hydrophilic film,. The commonly used surface head groups are thiol (-SH), silane (e.g. trichlorosilane -$SiCl_3$), and carboxyl groups (-COOH). The commonly used substrates are gold, silver, silicon and steel. There are many research studies of various SAMs having interaction with different substrate. The alkyl-silane SAMs on Si [20-25] and alkyl-thiol SAMs on Au [26-28] have been extensively studied. Progressively more, titanium based substrates are gaining importance. SAMs have been broadly investigated as a flexible tool for surface modification in various applications for example microelectronics, corrosion resistance and biosensors. They also facilitate studies of wetting, adhesion, friction and related phenomena [17].

There are various coating methods are used such as dip coating, spin coating and spray coating. Instead of these three coating methods dip coating method is used extensively because of its uniformity and cost effectiveness.

Friction and wear mechanism in polymer Tribology (coating of polymers on top surface):

In polymer tribology, friction between two sliding surfaces is generally affected by two terms, adhesion term and ploughing term [29].

(a) **Adhesion term:** is caused by the adhesive interaction of very low thickness layer of the polymer in contact with counter face.

(b) **Ploughing term:** is the result of plowing of the asperities of the counter face into polymer besides the sub-surface deformation involving plastic flow and fracture depending upon contact conditions.

If hardness of one of the sliding surface is very high relative to another surface, plowing term becomes important. The dependency of Adhesion term is the interfacial shear stress at the contact surfaces in the absence of hard asperities. Shear stress (τ) depends upon the contact pressure P as given in Equation (1) [30].

$$\tau = \tau_0 + \alpha P \qquad (1)$$

where τ_o is defined as the initial shear stress; α is the pressure coefficient; τ is defined as the friction force (F) divided by real contact area (A); P is calculated as the ratio of applied normal load (L) to real contact area (A) [31].

Thus Equation (1) can be rewritten as Equation (2) as given below.

$$F/A = \tau_0 + \alpha\,(L/A) \qquad (2)$$

Initial shear stress (τ_0) can be neglected in most conditions (especially high load conditions) [Briscoe and Tabor 1975]. Therefore, Equation (2) modifies as Equation (3) as follows.

$$F = \beta\, L \qquad (3)$$

Where β = μ (coefficient of friction) is the ratio of friction force to the applied normal load.

The polymers are visco-elastic in nature due to this nature its tribological behavior is more complex than that for metals or ceramics. For polymers, coefficient of friction depends upon load, contact geometry and loading time [30].

Tribology study in 21st century:

Current trends in research activity and technology, there are five areas of likely major activity in tribology over next few years

- Modeling and simulation
- Thin film lubrication
- Energy efficient technology
- Scientifically designed surfaces
- Smart systems

In above all the areas thin film lubrication is most important research in Micro-Electro-Mechanical Systems (MEMS) which makes a major constraint in MEMS applications. For reducing friction and enhancing the wear life a new method was investigated for MEMS lubrication known as Localized- Lubrication or “Loc-Lub”. PFPE is also most important lubricant in nano lubrication. The properties of this lubricant is describe below.

Use of PFPE as a lubricant:

In the early 1960’s, Perfluoropolyether (PFPE) lubricants were developed. It has been used as lubricants in different applications. A PFPE lubricant is a unique class of lubricants because of their versatile nature. PFPE lubricants have following useful properties:

- Good lubrication properties
- Low volatility
- Non-flammable
- Chemical inertness
- Low surface tension
- Excellent oxidative and thermal stability
- Effective in wide temperature range
- Non-cytotoxic and biologically inert
- Good radiation resistance

It has been applied as a top layer for improving the wear durability of different material tools [32]. So many researchers were observed that after applying PFPE as a top layer, coefficient of friction decreased and wear resistance of tool improved. These improved properties were attributed to the top layer of PFPE. For improving the wear life of monolayer's deposited onto Si based MEMS in a study we can use a mobile hydrocarbon-based lubricant as top layer also [33]. The tribological properties of UHMWPE films deposited on Si substrate are also improved by over coating of PFPE [34, 35].

Summary:

1. The nano-composite polymer coating as a boundary lubricant is found to be an effective way to reduce or eliminate the usage of harmful additives in the lubricating oils.

2. Under the severe boundary-lubrication condition, the nano-composite polymer film is found to be very effective in protecting the mating surfaces from wear under the base oil lubrication without any additives.

3. Titanium and its alloys are considered to be among the most promising engineering materials across a range of application sectors. Due to a unique combination of high strength-to-weight ratio, melting temperature and corrosion resistance, interest in the application of titanium alloys to mechanical and tribological components is growing rapidly in a wide range of industries, especially in biomedical field, also due to their excellent biocompatibility and good osseointegration.

4. The lubricious and bio compatible properties of the titanium and its alloyed DLC coating make it highly suitable for improving the performance of devices and micro devices for mechanical or biomedical application.

5. PFPE overcoat also reduces surface roughness of the substrate due to filling-up of surface texture by this nano-lubricant

6. UHMWPE coating on Ti6Al4V shows good tribological properties such as low friction coefficient and high wear life under tested conditions. Good mechanical and lubrication properties of bulk UHMWPE polymer resulted in useful tribological properties of this polymer coating.

7. If wear and friction properties are improved as well as a slightly differing lubrication mechanism, multiply-alkylated cyclopentanes or MAC lubricant has been proven to be an effective lubricant with compared to PFPE under reciprocating sliding wear conditions using ‘‘Loc-Lub.’’

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