Improving tribological properties of steels by surface texturing and coating

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Introduction

This thesis reviews the scientific contents and the experimental results relative to Ph.D. research activities carried out by the author at the Net-Lab SUP&RMAN (SUPerfici & Ricoprimenti per la Meccanica Avanzata e la Nanomeccanica, stands for: Surfaces and Coatings for High Advanced Mechanics and Nanomechanics), operating at the Dept. of Physics of the University of Modena and Reggio Emilia since 2004, under the scientific supervision of prof. Sergio Valeri.

The main keywords of the thesis coincide with the principal lines of interest followed by the Net-Lab researches: Tribology and Surface Engineering.

Tribology is literally the “science of rubbing”, and it could be defined as the full study of the interaction between surfaces in relative motion, whose state of the art of the knowledge is still far to guarantee an exhaustive comprehension of all the involved mechanisms. But despite their intrinsic complexity, tribological phenomena have always been considered crucial for human life, assuming a huge importance since prehistoric age when the wheel invention determined a considerable technological turning. The first clear scientific approach to tribology is attributed to Leonardo da Vinci: the deciphering of his works paved the way towards the formulation of the elementary and well known friction laws due to Amontons and Coulomb. Stimulated by the enormous industrial growth and consequent needing for energy saving and raw materials, during the last century tribology became a pivotal frontier to be explored in the contest of basic and applied physics at all scales (even atomic), and levels (from meso-systems to micro- and nano-devices, such as MEMS and store memories) where mating surfaces are involves and the minimization of friction and wear losses is required.

“Surface Engineering” is a novel expression that named the sub-discipline of material science dealing with the optimization of solid surface phase in order to functionalize the items during their interaction with the environment and the surrounding systems. From the technological point of view, Surface Engineering is meant to be considered an attractive instrument for tribological challenges: several solutions involving chemical, structural and morphological modification by means of adding material or reshaping surface topography, can be adopted with the aim of improving performances, reducing friction and wear, and/or increasing hardness and toughness.
This thesis is set in this field, and is oriented to give a contribute to the development of strategies and methods for the improvement of tribological properties of steel surfaces. Thus, steels suitable for specific industrial applications (mainly engine and automotive components) were chosen as substrates. The guideline of the experimental works follows two parallel Surface Engineering topics: surface coatings and surface texturing.

Applications of innovative hard “tribo-coatings” grown by “state-of-the-art” techniques (Physical Vapour Deposition-Magnetron Sputtering for thin films; Plasma Spraying and High Velocity Oxygen Fuel for thick layers) were studied, by carrying out various means of characterizations: mechanical (indentation), tribological (pin/ball-on-disk tests) and structural. In this last case, Dual Beam Machine - coupling a Focused Ion Beam (FIB) and a Scanning Electron Microscope (SEM) - was adopted in order to exploit its capability to guarantee simultaneous imaging and micro-machining approaches, trough which it is possible to perform “micro-cross section” analysis allowing to correlate the tribological behaviours to sub-surface microstructures. Related activities were performed in collaboration with the Dept. of Material Engineering of the University of Modena & Reggio Emilia.

Surface texturing involves modifications of surface topography, creating a uniform micro-relief with regularly shaped asperities or depressions. Nowadays, surface texturing delineates a scientific and technological open-frontier where the area of micro-fabrication converge to surface science committed to study and demonstrate the various mechanisms of integrated micro-effects resulting in a macro-benefit that optimizes performances. Tribologists have been investigated the impact of micro-texturing on mating surfaces since ‘60s, demonstrating by means of various experimental approaches and theoretical models that the presence of artificially created micro-irregularities can significantly affect sliding behaviours reducing friction, damping wear, and improving lubrication mechanisms. Among the various manufacturing techniques, Laser Surface Texturing (LST) offers promising peculiarities (fast processing time, clean to the environment, no need of vacuum, excellent and ease control of the shape and size of the ablated micro-textures by tuning the characteristic of the laser spot), and thus it was exploited to pattern steel surfaces by regular arrays of micro-dimples. A protocol of pin/ball-on-disk experiments was designed and then realized in order to quantify the tribological benefits ensured by micro-dimpling. Indeed, laser-steel interaction was investigated in order to detect “additional effects” due to LST in terms of locally confined morpho-structural modifications induced by laser heating (i.e. grain-size modification, hardening). Related activities were performed in collaboration with Technion Israel Institute of
Technology (Haifa, Israel) and with the spin-offs SurTech Ltd (Nesher, Israel) and FriCso Ltd (Tirat Carmel, Israel) which played a key role in LST manufacturing.

This thesis is structured as follow.

Introductive chapters briefly survey on history and basic principles of tribology (chapter 1), and Surface Engineering techniques (chapter 2), with a broader discussion focused on Surface Texturing. Remarkable works found in literature are highlighted in order to point out the scientific state of the art of the crucial topics: corresponding references will be quoted at the end of each chapter.

Further chapters are dedicated to the experimental results highlighting the contents of the papers recently published by the author [1-5].

Chapter 3 deals with the strategies of use of Dual Beam Machine, that deserves to be considered as a huge opportunity for tribology. FIB-based sub-surface characterizations carried out on plasma-sprayed TiO$_2$ coating [1] and “Duplex” DLC-based multilayers [2] grown on C40 steel are described in detail.

Tribological characterizations of laser micro-dimpled steels are treated in chapter 4. An intensive pin/ball-on-disk campaign carried out on 30NiCrMo12 textured steel [3] is reported: different lubrication configurations have been investigated in order to reveal the major integrated effects due to micro-dimpling (oil-holding capacity, additional hydrodynamic lift, trapping wear debris). The last paragraph of chapter 4 introduce the preliminary study [4] regarding laser micro-dimpled 20MnCr5 steel coated by an hard thin CrN film.

Chapter 5 is dedicated to the sub-surface characterizations of laser-textured steel [5]. Both, FIB-based and AFM-based analysis will be discussed through a new theoretical model developed in collaboration with prof. Nicola Pugno (Dept. of Structural Engineering, Polytechnic of Turin).

Conclusions and future perspectives of works have been added.
Author’s reported papers


Chapter 1

History and fundamentals of tribology

1.1 Tribology

The word “tribology” derives from the Greek binomial “Τριβοσ” (“tribos”: meaning “rubbing”) and “λογοσ” (“logos”: meaning “principle” or “logic”): thus, the literal translation would be the science of rubbing [1]. A more suitable definition could be stated as the full study of the interaction between surfaces in relative motion: it spans many disciplines, from physics and chemistry to mechanical engineering and material science, including its extreme technological impact and importance [2]. Recently, this discipline had been a huge development, becoming a pivotal frontier to be explored in the contests of basic and applied Physics. However, the history of tribology is ancient.

Figure 1.1: Egyptian picture (1880 BC): use of a sledge to transport a heavy statue [3]. A man on the sledge helps the sliding pouring a liquid into the path of motion.

The earliest experiences encountered in this field are placed in prehistoric ages due to the firsts tool manufacturers, sculpting bones and metals. Remarkable pioneering traces could be retrieved even in ancient Egypt. The famous picture reported in Fig. 1.1 (datable around 1880 BC) portrays 172 slaves dragging a monolithic statue (estimated weight: 600 kN) along a wooden skid. A standing man is recognizable on the plinth: he is pouring a liquid into the path of motion,
Chapter 1 - History and fundamentals of tribology

deserved to be considered a forerunner lubrication engineer [4]. Nevertheless, the wheel invention determined a huge progress, reducing friction (from grazing to volving) occurring in transport mechanisms.

The first scientific approach to tribology is ascribable to the renaissance Italian engineer-artist Leonardo da Vinci (1452-1519), who was the first to enunciate two laws of friction (about two centuries before Newton even defined what force is!): the deciphering of his work [5] took several centuries, and had been a milestone for the subsequent development of this branch of science. Other famous earliest tribologists were the French physicists Guillaume Amontons (1663-1705) and Charles Augustin de Coulomb (1736-1806) who made similar observations than da Vinci’s ones [6,7], the English chemist Charles Hatchett (1760-1820) who carried out a first experimental campaign using a simple reciprocating machine in order to evaluate wear on gold coins [8], and the French inventor-natural philosopher John Theophilus Desaguilers (1683-1744) whose contribute was fundamental regarding the improvements upon firsts steam engines [9].

However, the term “tribology” became widely used only in the last century, in coincidence of the enormous industrial growth. At present, the state of the art of the knowledge is far to guarantee a definitive and exhaustive comprehension of the mechanisms of friction and wear, but lots of progresses have been made due to the several efforts recently spent in research. Thus, nowadays tribology is meant to be crucial for the scientists, especially due to the considerable impact on modern machinery which is based on sliding and rolling contacts. Examples of productive wear could be found in domestic procedures, such as writing with a pencil, washing the dishes, machining and polishing. Forms of productive friction govern the biomechanics of human body, and the operation of brakes, clutches, driving wheels on trains, cars, bolts and nuts. Conversely, the most common types of unproductive friction and wear afflict internal combustion and aircraft engines, gears, cams, bearings and seals. Drafted in 1966, the Jost Report [10,11] was the first official document traducing annual tribological losses in energetic and economic wastes: according to its esteem, U.K. could save approximately £500 million per year, and the U.S. could save in excess of $16 billion per year by better tribological practices. In other words, it means that one third of world energy resources are wasted in friction dissipations, wear and corrosion forms. These conclusions oriented the scientific and technological communities towards the needing of strategies for friction reduction and wear control. Economic perspectives and long-term reliabilities (i.e. energy and matter savings) gave a fundamental lift towards the wide diffusion of tribology, justifying the birth of several national and international centers for tribology, and the training of high-quality tribologists whose main purpose of research is the minimization and elimination of
losses resulting from friction and wear at all levels of technology where mating surfaces are involved. Therefore, the results in this discipline lead to optimize the efficiency of the systems obtaining higher performances, fewer breakdowns, and significant savings.

Tribology started to be deepened studying the phenomenology of interacting macro/meso-systems, characterized by large masses and heavy applied loads (comparable to the human life cases), where bulk materials are involved and inevitably worn. In the last decades, the development of the microscopic devices (store memories, Micro Electro Mechanical Systems -MEMS-, etc.) forced tribology to move towards the nano-scale, and to assume a new importance and interest. Consequently, the so-called micro/nanotribology born with the intent to explore new frontiers dictated by smaller masses and loads (down to µNs or nNs). When the dimensions of the systems are reduced, the surface forces become stronger than bulk forces, and so friction and wear are related to the interaction of thinner surface layers (even consisting of few atoms in such reproducible cases). Indeed, related phenomena such as adhesion and lubrication follow different behaviours due to the confinement of the contact. The extension of the range of the tribological investigations opens several classes of problems related to the scaling gap. The advent of new techniques to measure topography, adhesion, friction, wear, lubricant film thickness, and mechanical properties, all on meso- to micro- to nanometer scales, led to the development of the respective sub-fields of the tribology, separated by different approaches and laws that govern and explain the interfacial phenomena. Providing a bridge among them is a tough challenge towards a fundamental and complete understanding.

A final heuristic comparison could help to individuate the two limit cases of well studied tribological systems. It is known that a sharp edge of a tip-based microscope slides on a surface reproducing a single asperity contact, while at the interface of meso/macroscopical systems contact occurs as an integration of multiple asperities junctions. The research lines followed during the three year Ph.D. experience match in the middle between the former and the latter scenario. No nano-objects had been investigated, neither AFM/FFM (Atomic Force Microscope/Friction Force Mode) experiments had been carried out: the mechanics of the single asperity contact is beyond the goal of this thesis work. The typical experiences performed by the author regard the multiple asperities contact scenario, but the mating systems as studied present micrometrical surface modifications such as micro-cavities and/or coatings which effects will be discussed later.

Taking into account the mentioned guidelines of thesis researches, a bird’s eye summary of the main aspects of the tribology at the macro-scale will be illustrated in the next paragraphs. Three key topics will be discussed: friction, wear and lubrication.
1.2 Friction

Friction is the force resisting the relative motion of two solid surfaces in contact (or a solid surface in contact with a fluid), that converts kinetic energy into thermal energy or heat. It derived from electromagnetic forces between atoms and electrons: contrary to popular thought, it is not caused by surface roughness but basically by chemical bonding between mating surfaces although it has been demonstrated that surface roughness and contact area afflict sliding friction for micro- and nano-scale objects where surface area forces dominate inertial forces [1]. Thus, friction is not a fundamental force and so, due to its nature, it cannot be calculated from first principles but instead must be yielded empirically.

The first attempt of developing a theory started with the experiences of Leonardo da Vinci, datable across the end of fifteenth century and the beginning of sixteenth century. He studied the sliding of blocks on inclined plane, varying blocks masses and angles of inclination. He derived the definition of static friction measuring the load and the inclination necessary to start the block motion, and he observed the independence of friction from the extension of the contact area between the sliding blocks and the inclined surface [5].

In 1699, G. Amontons formalized three conclusions [6]:

- The friction force linearly depends only to the applied load and not on the extension of the contact area;
- The resistance caused by rubbing is more or less the same for iron, lead, copper and wood in any combination if the surfaces are coated with pork fat;
- The resistance is more or less equal to one-third of the applied load.

Essentially Amontons formulated the well known expression for friction force (Amontons Law):

\[
F_f = \mu N
\]  

(1.1)

where \( F_f \) is the friction force, \( N \) is the applied load and \( \mu \) is the friction coefficient empirically determined. Later (1773), C.A. Coulomb made the first clear distinction between static and kinetic friction and published some experimental results about metal and wood [7]. His contribute was completed with the formulation of the well-known Coulomb’s law:

- Kinetic friction is much lower than static friction and is independent to the sliding velocity.
The friction coefficient is not a well-defined parameter, and a prediction of its value is impossible for any given system. Hence, experimental tests are necessary to fill material tables, but on the other hand it is clear that friction coefficient could not be known exactly because it always strongly depends on the experimental conditions. Therefore, although it has to be considered a good approximation for macroscopic related phenomenology, the simplest relationship expressed in eq. (1.1) is far from an exhaustive description of friction.

In 1950, Bowden and Tabor theorized that the friction dissipation is a consequence of the sum of plastic deformations of the asperities during sliding under high pressure contacts. They definitely opened the debate about the not negligible adhesion between asperities, a topic already introduced by the rough speculations due to J.T. Desaguliers [9]. The main Bowden-Tabor work introduced the argument of the real contact area to explain the independence of friction to the apparent contact area [12]: the projection of the surface of one mating body on the other one is several order of magnitude larger than the sum of the areas of the contacting asperities. Therefore, the eq. (1.1) must be rewritten in the well recognized fundamental equation of friction:

$$F_f = \tau A_r$$

(1.2)

where $A_r$ is the actual contact area, and $\tau$ is the shear modulus (i.e. the friction force for area unit). This approach does not explain the linear relationship between friction force and applied load, but could be well adopted for all the macroscopic systems.

In 1966, Greenwood and Williamson [13] reconciled eq. (1.1) and eq. (1.2). Starting from the more simplified theory of Archard [14,15], they developed a statistic theory of multi-asperity contact regime, based on a model that described the two contact surfaces trough three parameters: the asperity density, the standard deviation of asperity height distribution (exponential and gaussian), and the asperity radius (first assumed to be hemispherical, later changed in a gaussian distribution [16]). This theory led to the conclusion that the ratio between contact area and load (and consequently between friction force and load) is linear. Other more complex theories with different distributions of asperity height and density, and with different asperity apex shapes, have been recently developed. None of these denies the linear dependence between contact area and load.

The weakness of the Greenwood-Williamson model is in neglecting the adhesion contribute at interface. Thus, several further theories have been developed in order to take into account the roughness-adhesion connection, from Fuller-Tabor theory [17] to Persson-Tosatti approach [18] that works with self-affine surfaces (especially in this case roughness reveals a strong influence on
adhesive forces). In a simplified description the adhesive term could be introduced directly into the Amontons Law (eq. (1.1)):

\[
F_f = \mu (N + F_0) \approx k + \mu N
\]  

(1.3)

where \( k \) is a constant friction force due to adhesion, and \( F_0 \) is a constant adhesion force which nature is the sum of different components: Van der Waals forces, electrostatic forces, capillary forces (or meniscus effects), chemical bonds, acid-base interactions.

As mentioned above, reducing the scale of contact the interface mechanics changes dramatically. Several single asperity theories has been developed, based on different geometrical assumptions, including or neglecting the adhesion contribute and other short-range interface forces. All of them implies a power law relationship between applied loads (\( N \)) and contact areas (\( A_R \)).

The simplest, and thus most famous and widest used one is Hertz theory (1881) that describes the perfect elastic, non adhering case of the contact between two spheres of radii \( R_1 \) and \( R_2 \), Young moduli \( E_1 \) and \( E_2 \), Poisson’s ratios \( \nu_1 \) and \( \nu_2 \), related trough [19]:

\[
\begin{align*}
A_R &= \pi \left( \frac{\bar{R}}{K} \right)^{2/3} N^{2/3} \\
\bar{R} &= \frac{R_1 R_2}{R_1 + R_2} \\
\frac{1}{K} &= \frac{3}{4} \left( \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \right) 
\end{align*}
\]  

(1.4)

Other common single asperity contact theories are extensions or improvements of the Hertz theory such as Johnson-Kendall-Roberts (JKR) that describes sphere-flat coupling including adhesion forces [20], and Derjaguin-Muller-Toporov (DMT) that includes a Lennard-Jones potential interaction at interface [21].
Measuring friction at macro-scale

Some of the earliest friction test-rig were done by an arrangement of pulleys and weight (Fig. 1.2 (a)) allowing the measurements of static (at start of the motion) and kinetic (at uniform sliding velocity) coefficients of friction. A second convenient system is the already mentioned “da Vinci’s strategy”, using an inclined plane as path of motion (Fig 1.2 (b)).

![Figure 1.2: a) Simplified sketch of an earliest friction test-rig: an arrangement of pulleys and weight allows to measure static and kinetic friction coefficients. b) Representation of the “Da Vinci’s strategy”: the study of the sliding of blocks on inclined plane by varying blocks masses and angles of inclination [2].](image)

Presently, the most commonly used machine to measure friction force between macro/meso-scale mating bodies is the tribometer. It consists in a combination of various devices such as simple spring scale and transducer that produces an electrical signal proportional to applied and lateral forces. The deflection of the holder of one of the contact bodies (typically the static counterpart) can be measured by capacitance sensors, piezoelectric materials, optical interference, moiré fringes, light beam deflections and several other methods.

There are many sensing strain gages available, and also many designs of tribometers ranging among different features, structural modes, and contacting configurations. Tribometers can be classified in terms of range of load, range of speed, working ambient in which they work, type of generated motion (reciprocating, continuous, rotating, linear), geometry (round/spherical, cylindrical, flat) and shape (ball, pin, block, ring) of sliding members.
In particular, pin-on-disk configuration reproduce a flat-on-flat contact. Ball-and-disk configuration is quite similar, but it reproduces a round-on-flat contact, where the relationship between real contact area and applied load could be approximately estimated by Hertzian approach (eq. (1.4)).

These just mentioned geometries (Fig. 1.3) imply a flat or round tip held by a cantilever-shaped force transducers (typically a cell force or a strain gage supported by shock absorbers) when sliding against a disk usually rotated by a drive system.

![Diagram](image)

**Figure 1.3:** Scheme of a pin/ball-on-disk tribometer and its principal components. a) Top view. b) Side view [2].

Two different pin/ball-on disk tribometers (see Fig.1.4, and Tab. 1.1) have been used for the experimental campaigns that will be detailed in the next chapters. The related discussions about the experimental results will take into account the considerations as mentioned in paragraph 1.1: pin/ball-on-disk dynamic tests could be assumed to reproduce multi-asperity contact.

Thus, the linear dependence between loads and real contact area will be assumed, and due to the high applied loads (ranging from fraction of Newtons to tens of Newtons), the adhesion contribute will be neglected (referring to eq. (1.3): \( k << \mu N \)).
Figure 1.4: a) TRN tribometer (provided by CSM Instruments®); b) UMT2 micro-tribometer (provided by CETR®); both pin/ball-on-disk apparatus are located at Net-Lab SUP&RMAN (Univ. of Modena and Reggio Emilia – Dept. of Physics) and were adopted for the experimental campaigns will be detailed in the next chapters.

<table>
<thead>
<tr>
<th></th>
<th>CSM® - TRN</th>
<th>CETR® - UMT2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range of applied load</td>
<td>1 - 10 N</td>
<td>1 mN - 200 N</td>
</tr>
<tr>
<td>Range of sensor force</td>
<td>0.1 – 20 N</td>
<td>5 mN - 200 N</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 mN – 500 mN →</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FL sensor</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05 – 5 N →</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DFM sensor</td>
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<tr>
<td></td>
<td></td>
<td>2 – 200 N →</td>
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<td></td>
<td></td>
<td>DFH sensor</td>
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<td>Range of rotor speed</td>
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<td>measurements</td>
<td></td>
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<tr>
<td>Atmosphere control</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Compatible probes</td>
<td>Pin, ball</td>
<td>Pin, ball</td>
</tr>
</tbody>
</table>

Table 1.1: Main characteristics of the tribometers.
1.3 Wear

Wear is defined as the phenomenon of material removal from a surface due to interaction with a mating surface, and is the main reason of losing in durability and reliability of almost all machines. Wear could be seen as the result of different processes triggered by the sliding contact between two surfaces, such as physical separation due to microfracture, chemical dissolution and film formation, interface melting generated by frictional heating. Thus, wear is an unstable character of each “tribo-system”, and it could change dramatically even with a relatively small perturbation of dynamic, environmental and material parameters: as Bayer correctly stated, “wear is not an intrinsic property, but a system response” [22].

Tracks of removed material, surface roughness, shape and consistence of produced debris give important information in characterizing wear, that is generally quantified evaluating the amount of volume lost and qualified by the state of worn surface. Specific wear rate is defined as wear volume per unit of slid distance and unit of applied load on mating surfaces. Due to the huge complexity of the topic, no complete and exhaustive theory could resolve and predict all the possible wear behaviours. Indeed, the well accepted approach to study wear cases is based on the classification of wear mechanisms, even if they are not always well differentiated but often interrelated, and their understanding sometimes seems to be confusing and difficult.

Figure 1.5: Descriptive keywords of wear and their interrelations [23].
Wear modes

The scheme in Fig. 1.5 summarizes the main descriptive wear keywords. Wear types could be correlated to the contact types: sliding, rolling, impact, fretting (a form of repetitive and reciprocating sliding), and slurry (with powder as counterpart).

Therefore, a better classification (generally recognized as fundamental) is the distinction among wear modes based on the knowledge of deformation states, and thus of the mechanics that governs the contact. Following this latest classification due to Burwell [23], four major wear modes could be distinguished (Fig. 1.6):

- Adhesive wear (Fig. 1.6 (a)): if the interface between two surfaces is generated by a plastic contact characterized by enough adhesive bonding strength to resist relative sliding, large plastic deformation caused by dislocation is introduced under compression (at entrance) and shearing (at exit). As a result of such large deformation in the contact region, cracking phenomena are generated by mechanically induced stresses and strains, and thus they propagate in the combined fracture mode of tensile and shearing. When the crack reaches the contact interface, wear particles are formed and adhesive transfer is completed;
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• Abrasive wear (Fig. 1.6 (b)): if the scenario is similar than previous one, but the plastic contact occurs between hard and sharp or soft material, the harder penetrates to the softer one and an interlock takes place generating ploughing. A cut and scared groove is usually formed. In particular, when wearing material has ductile property, a ribbon-like long debris is generated by a sort of microcutting; while instead in the case of brittle material, wear particles are generated by crack propagation. Thus, in this contest, hardness and stiffness properties of the two mating surfaces are extremely correlated to the wear behaviour;

• Fatigue wear (Fig. 1.6 (c)): if it occurs after repeated friction cycles on both elastic and plastic contacts. Neither adhesive and abrasive mechanisms are involved: deformation, crack propagation, comparison of wear particles, and, in such cases, complete surface failure are stochastic consequences of prolonged running-in states of work generating a certain number of repeated contacts;

• Corrosive wear (Fig. 1.6 (d)): if the material removal is not governed by mechanical interaction, but rather by the growth of chemical reactions (the most representative one is the oxidation, and in that case it is not wrong to talk about oxidative wear). These are highly activated and accelerated by frictional deformation, frictional heating, microfracture and successive reaction products that in such cases end up to strongly adhere to the surfaces forming a reaction layer.
1.4 Lubrication

Lubrication may be defined as a strategy of controlling friction and wear interposing a solid, liquid or gaseous media between interacting surfaces in relative motion under load. As da Vinci observed about five centuries ago, “all things and anything whatsoever, however thin be, which is in the middle between objects that rub together lighten the difficulty of friction” [2].

The equations that describe lubrication with continuous fluid films are derived from the basic laws of fluid-dynamics through progressive, ad hoc, and more and more complex specialization to the particular geometry of lubricant film, contacting surfaces, as well as boundary conditions and flow conditions. The most commonly used methods in lubrication modelling decline the so-called Navier-Stokes equations [24-26] that govern the motion of an incompressible, lubricant flow characterized by a velocity vector \( \vec{v} \) and a constant viscosity (\( \eta \)):

\[
\rho \left[ \frac{\partial \vec{v}}{\partial t} + (\vec{v} \cdot \nabla)\vec{v} \right] = -\nabla p + \eta \nabla^2 \vec{v} + \rho \vec{f} \\
\text{div} \, \vec{v} = 0
\]  

(1.5)

where \( \rho \) is the lubricant density, \( p \) is the internal pressure and \( \vec{f} \) is the generic external force field vector for unit of volume.

However, due to the complexity of the topic, the study of lubricated contacts needs more simplified approaches. Thus, a realistic approximation allow to distinguish three major lubrication regimes: hydrodynamic (or full fluid), elastohydrodynamic, and boundary (Fig. 1.7).

![Figure 1.7](image)

**Figure 1.7:** Schematic representation: the contact topographies referred to the three major lubrication regimes [2].

When the contact geometry and operating conditions are such that the load is fully supported by a fluid film, the surfaces stand completely separated. This is generally referred to as the hydrodynamic lubrication (HL) or full fluid lubrication regime, where deformations of mating bodies are negligible and their reciprocal sliding is mediated by a viscous friction force that could...
be approximately considered as linear with the sliding speed. A related theory for fluid film design has been well developed: it is based on Reynolds’ equations and continuum mechanics [27], that assume laminar flow and combine the equation of motion and the continuity equation (eq. 1.5) into a single equation in lubricant pressure.

Increasing the load and/or reducing the speed, the hydrodynamic pressure may not be sufficient to fully support the load, and the surfaces come into contact. The contact occurs at the peaks and hills of the surfaces. The amount and the extent of these asperity contacts depend on many factors: surface roughness, hardness and elasticity of mating bodies, fluid film pressure, applied normal load. Many of the asperities undergo elastic deformation under the contacting conditions, thus the normal pressure is balanced by both the asperities strength and thinner fluid film lift. This condition is generally referred to the elastohydrodynamic lubrication (EHL), whose related theory [28] is due to Dowson and Higgingson (1959). EHL theory is capable to describe surface temperature instabilities, fluid film thickness and pressures, but it does not take into account the eventual chemical transitions neither wear and the presence of the so-called “third body” (wear debris).

Further increase in the contact pressure (and/or decrease in the speed) beyond the EHL regime causes the tightening of the tribological conditions. Deformations of contact asperities increase: the number of junctions increase and related stress distribution changes as well as the fluid film thickness decrease since below the average surface roughness. Thus, surface contact becomes the major part of the load supporting mechanisms, and both plastic and elastic deformations occur. Mechanical interactions produce wear, abrasion, adhesion and fatigue under sliding conditions, and even chemical reactions between asperity surface and lubricant molecules could be activated by frictional heating often producing a boundary film, that can be either beneficial (i.e. protective, benign, antiwear) or detrimental (i.e. prowear) in terms of wear [29]. The combination of the load sharing by the asperities and the occurrence of chemical reactions constitutes the lubrication regime commonly named boundary lubrication (BL). Inside this contest, a comprehensive full theory is still lacking: physical and chemical processes involved are not well understood, even if some models on lubricant chemistry and contacts mechanics do exist [30,31], in some cases recently developed through molecular dynamic simulations [32].

It is crucial but not trivial identify the thresholds of the lubrication regimes, where the HL or EHL end, and BL begins. Therefore, almost all practical systems do not work in pure EHL or BL, but rather in a more or less extended mixed lubrication regime because of the broad or sharp asperity height distribution. Thus, the deformation of each individual asperity ranges among soft,
elastic and elastoplastic. As wear accelerates and chemical reactions occur, surface topography also evolves: surface conformity can either develop or disappear, the actual contact area and, hence, the asperity stress distribution also changes.

**Stribeck curve**

As explained above, modelling and prediction of lubrication regimes are complex, and an unique description of lubricated sliding systems is not always coherent due to the instabilities of the processes involved. A simplified but almost useful approach in describing lubricated contact implied an empirical and phenomenologic relationship between friction coefficient and tribological conditions. A curve attributed to Stribeck [33-35] portrays the variations in friction over a range of the so-called Stribeck parameter (or Stribeck number, or Sommerfeld number) defined as the ratio $\frac{\eta U}{W}$, where $\eta$ is the lubricant viscosity, $U$ is the sliding speed and $W$ is the nominal contact pressure between mating bodies. This approach allows to estimate the likelihood of surface damage, such as the adequacy and the effectiveness of lubrication, quantifying the thresholds of lubrication regimes with an empirical approach.

The weakness of this approach is in neglecting the actual thickness of the lubricant film, and even its relationship with the corrugations of mating bodies. An alternative, and thus complementary approach consist in the $\Lambda$-curve, where friction coefficient is plotted against a dimensionless parameter calculated as the ratio between the effective film thickness ($h$, that depends on speed, load and viscosity) and the square root of the summed arithmetical roughness of the two contacting surfaces ($Ra_1, Ra_2$):

$$\Lambda = \frac{h}{\sqrt{(Ra_1)^2 + (Ra_2)^2}}$$  \hspace{1cm} (1.6)

However, effective lubricant film thickness is far from trivial to be measured in practice during running-in tests. For this convenient reason $\Lambda$-curve approach is not usually adopted although it is based on a more complete parameterization taking the roughness into consideration. Then, Stribeck approach is more preferably used. A typical Stribeck curve is shown in Fig. 1.8. Three regions of the curve could be distinguished and correlated to different behaviours of the lubricated “tribo-system”.
At the right part of the curve, friction increases almost linearly with $\frac{U}{W}$ ratio: within this condition (high speeds, and/or low loads, and/or consistent film viscosity), is reasonable to assume that lubricant film is thick enough to fully support normal pressure during sliding. Therefore, junctions and consequent deformations are negligible, and dissipation due to friction must be ascribed only to viscous losses. Thus, this region of the curve could be associated to HL regime (or full fluid). Diminishing $\frac{U}{W}$ ratio, friction coefficient reaches a minimum, more often in the form of a large plateau: the lubricant film thickness is reduced as well as the viscous dissipations, revealing the limit of HL regime, and thus the beginning of EHL and/or mixed regime. Consequently, for lower $\frac{U}{W}$ ratios, tribological conditions become tighter: asperities collisions start to be less and less negligible. Indeed, contacting bodies are thought to be supported on a mixture or combination of asperity-asperity adhesion joints, and fluid regions between asperity. The left-hand section of the curve is associated to the most consistent transition between mixed and boundary lubrication regimes: the fluid-dynamic lift vanishes as lubricant molecular bonds go breaking and a detrimental “third body” accumulates between the counterparts. Thus, friction coefficient rises up to the quasi-static values in correspondence of low-limit $\frac{U}{W}$ ratios (i.e. critical pressure, and/or vanishing sliding speed).
1.5 References

[26] Szeri AZ, *Fluid Film Lubrication, Theory and Design*. Cambridge (1988);


Chapter 2

Surface Engineering: a brief survey of techniques

2.1 Classification

Solids are composed of a bulk material (bulk phase) bounded by a surface (surface phase) that acts as an interface to the environment. The expression Surface Engineering named the sub-discipline of materials science which deals with the modification of surface phase. Surface Engineering involves altering the properties of surface phase in order to optimize its function during the interaction with the surrounding systems. Surface Engineering consists in the study and development of technologies and techniques principally aimed to the improvement of physics and chemistry of material, electrical engineering (particularly in relation to semiconductor manufacturing), and mechanical engineering (particularly in relation to high-performance components).

Because of the growing need for energy saving and raw materials, the functionality and the lifetime of finite products must be enhanced. Propelled by these crucial reasons for social life, Surface Engineering finds more and more applications and interests in a wide range of industrial sectors. The principal are: automotive, aerospace, missile, power, electronic, biomedical, textile, petroleum, petrochemical, chemical, steel, power, cement, machine tools, construction.

Thus, the state of the art of Surface Engineering advances following the direction of capillary and multidisciplinary specialization, because a rich alternative of technologies is required in order to overcome the challenges of volume production. More and more techniques have been implemented in order to satisfy all the industrial requests: cheapness, flexibility, manufacturing capability on different scales (typically from micro- to nano-). Each class of techniques is aimed to become mostly suitable to a specific class of materials and applications, and could represent a highly sophisticated solution for a specific class of problems. Although a complete and exhaustive review is quite impossible to draw up because of the extensiveness of the topic, this chapter will propose a classification of most of the existing Surface Engineering techniques, deepening the description of those adopted during the Ph.D. research activities.
Surface Engineering techniques are used to develop or improve a wide range of functional properties (including: aesthetic appearance, biocompatibility, adhesion, wettability, mechanical resistance, heat barrier, corrosion protection, wear resistance and friction control) wherever the performances of an item need to be enhanced, or in such cases to restore original dimensions, to salvage or to repair an item. It is necessary to premise that every possible classification will never be rigid and strict. Indeed, due to their characters of versatility and flexibility, almost all the principal techniques are not mutually exclusive, but rather complementary and interrelated one another.

**Figure 2.1:** Tree diagram: the families of Surface Engineering techniques.
The diagram in Fig. 2.1 summarize a collection of the mostly widely used Surface Engineering techniques grouped in a sort of family tree. Principal Surface Engineering techniques could be roughly classified between two families: surface finishing and surface texturing. The latter basically involves topographical modifications through various manners of surface reshaping, while the former typically regards structural modifications by addiction or removal or chemical alteration of material.

### 2.2 Surface finishing

The term “surface finishing” is used to describe a number of industrial processes that can be applied to improve a manufactured item, covering its surface, or changing its chemical composition, or altering its sub-surface microstructure. A further classification is in distinguishing three kind of surface finishing: modification of the chemistry, removal of material, addition of material.

Principal processes based on chemical alteration are listed below:

- **Hardening**: it consists in a mechanism of forging and infusing elements into the material surface, forming a thin layer of a harder alloy gradually decreasing further from the surface in order to increase hardness, toughness and mechanical resistance [1]. The mechanism could be activated by heat sources (such as flames, furnaces, or laser beams) or by exposure to an oscillating magnetic field (induction hardening).

- **Diffusive methods**: they exploits thermodynamic reactions based on transport phenomena by convection, and they are typically applied to iron, iron-based alloys, and steel in order to achieve and exploit the direct formation of hard composite ferrous phases combined with suitable elements (C, N, B or a mixture of them). They are increasingly used to improve wear behaviour, hardness, load-bearing capacity, and in limited cases corrosion resistance [2,3]. The most important diffusive method is Carburizing (or Carburization), that works via the implantation of carbon atoms into the surface layers by a heat treatment below the melting point (temperatures between 800 °C and 900 °C) in the presence of a solid (in the case of charcoal the process is known as cementation, an obsolete technique), liquid, gaseous material, or plasma source (typically methane-based) which decomposes so as to liberate carbon when heated.
Similar to the Carburizing is the Nitriding (or Nitridization) that consists in the enrichment of the surface layer by nitrogen alone. In this case the treatment takes place in a thermal salt-bath, or in a plasma environment (typically ammonia-based) where the reached temperature ranges among 500-600°C, below the eutectoid threshold of Fe-N phase-system. Other affine processes involves the transfer of boron (Boronizing) or the mixed diffusion of a mixture of carbon and nitrogen (Carbonitriding or Nitrocarburization).

- Passivation methods: they include all the process of making chemically inert (“passive”) a material in relation to another one prior to interact them together. They are often based on galvanic procedures, or in some cases on electroless recipes involving aqueous bath and acidic attacks. In the most significant cases, passivation processes induce the spontaneous formation of a hard non-reactive surface film (few atoms thick) that inhibits corrosion. This layer could be composed of phosphates (Phospating), chromates (Chromatizing) and oxides (Oxidation), in relation to the passivated material and to the type of process. Anodizing is the most common oxidation process exploited to increase hardness, corrosion and wear resistance, and to provide better adhesion and lubrication. As the name suggest it involves the application of anodic electrochemical reactions to form a natural oxide layer [4].

Strategies of removing material are usually adopted to provide surface smoothing, reducing roughness, eliminating asperities, morphological defects and chemical impurities, and in such cases compacting and reinforcing the top layer. The principal surface finishing processes involving the removal of material are well adopted in the industrial context of manufacturing item, and they basically regroup all the procedures of polishing and lapping, from the roughest to the most sophisticated and refined.

Among these, deserve a mention [5-7]:

- Grinding consists in the primary and preliminary processing to reach the surface finish of manufacturing workpieces (typically metal-based). It is a purely mechanical treatment exploiting the use of a surface grinder, a machine tool from whose critical size depends the degree of precision processing (typically reaching micrometers).
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- Buffing indicates a class of further mechanical finish methods, to break down the roughness (even to nanometers) and to make the surfaces satin, bright and even mirror-like smooth, exploiting the use of abrasive papers (typically SiC-based), belts, wheels, and pads often imbued with opportune emulsions, suspensions or foams (typically alumina-based).

- Pickling indicates a class of chemical methods to remove impurities, stains, rust or scale via an acidic attack (typically sulfuric, hydrochloric, nitric or hydrofluoric). It is usually adopted for metal and steel (principally low carbon-based) as pre-processing before successive addition of material (painting, plating or galvanization).

- Electropolishing contemplates the use of electrochemical and galvanic processes aimed to degrease, polish, passivate and deburr surface top layers of conductive materials. It is often describe as the reverse of Electroplating and Anodizing because the purpose is not to grow a protective film or to induce the oxidation, but rather to erode matter, smooth and clean.

- Flame polishing is a method usually adopted for flattening thermoplastics or glass by exposing them to a flame or heat in order to achieve the melting point of the surface, and thus allowing the internal tension to release smoothing the surface out.

- Sandblasting is a generic term for the process of smoothing, shaping and cleaning a hard surface by forcing solid thin particles (typically silica-based dusts or powders) across that surface at high speed.

- Shot peening is a process based on shock-impulsive dynamics where a repetitive flow of balls (typically made of steel, with diameter ranging between 0.2 mm and 2 mm) with sufficient kinetic energy impacts the item in order to alter its sub-surface microstructure. In addition to flattening, it causes plastic deformation resulting in increasing hardness, and in the alignment of compressive stresses to be formed just below the top layer, helping to suppress fatigue wear and cracking phenomena [2].

The third and last classes of surface finishing methods regroup all the coating technologies that provide an addition of a new material above the exiting one, creating an interface-joint, more or less gradual, in order to physically separate the vulnerable substrate from external damage processes. Discrete coating technologies range from open-air to more sophisticated vacuum-based.
Open-air coating technologies are principally classified between liquid-state and dry-state. The latter sub-group comprehends all kind of welding and cladding methods, which consist in the joining of a flat and thick sheet of molten material placed onto a substrate in a series of adjacent layers or strips [2]. The former sub-group basically involves two types of peculiar methods:

- **Painting**: it consists in the application of an organic mixture (paint or varnish) constituted by pigments, extenders, dryers, and other special additives meshed in a solvent, directly streamed at the surface. The droplets merge on impact to form a liquid film, that solidifies according to the surface tension forces, and through polymerization reactions governed by the exposition to atmospheric oxygen and UV-light. Painting is used to preserve, decorate, and more frequently to retard corrosion, or to add functionality such as modifying light reflection or heat transfer properties [8].

- **Electroplating**: it consists in the grow of a protective plate (basically anti-wear or anti-corrosion) induced by an electrochemical reaction in a galvanic environment. A conductive item (works at cathode) is placed in an aqueous solution of a salt of the coating metal whose source is supplied with a strong electric potential (at anode). Cathodic reactions lead to the reduction of metal from solution, and to the evolutions of hydrogen and oxygen allowing to capture free metal ions electrically fluxing from the anode where they dissolve [9]. Although they still have a wide use in industrial applications due to its cheapness, practicality and fastness, electroplating methods start to be considered obsolete principally because of the environmental impact correlated to the disposal of waste liquid. Indeed, the quality of electroplate coatings is discussed: they tend to be rich in hydrogen, and its presence often causes microstructure problems such as brittleness. Another trouble of electroplate coating is the lack of uniformity due to the complex process of film formation, governed by the strength of electric field such as locally instable for morphological reasons: thus, corners, edges, projections are coated more rapidly than plane surfaces. Essentially, electroplating impose severe limitations on the range of coating materials and on the physical shape and size of the coated component [2].

The new frontier of discrete coatings move towards the replacement of the electroplating methods through much more versatile open-air technologies dry-state based for thicker coatings (Thermal Spraying - TS, and Plasma Spraying - PS), and much more sophisticated vacuum-based
technologies for thinner coatings (Physical Vapour Deposition - PVD, and Chemical Vapour Deposition - CVD).

### 2.2.1 Thermal and Plasma Spraying

Plasma and Thermal Spraying lead the major class of dry state-based coating techniques offering a fast and convenient manner of growing thick coatings of metals and ceramics on almost any shape of substrate by high deposition rates. Thermal and Plasma Spraying techniques exploit the painting principle, applied to a stream of solid thin particles or powders raised to several thousand degrees Celsius, so that any material (even refractory ceramics and aluminum oxide) could be melted and sprayed onto the substrate in a liquid state before cooling to merge and form a solid continuous layer (Fig. 2.2). The principal limitations are ascribed to the substrate, that must be sufficiently massive and characterized by a moderately high melting point, because of the heat absorption from the molten coating droplets: this excludes polymers and low melting point metals, but apart from these few restrictions Plasma and Thermal Spraying techniques found a broad range of applications, principally anti-wear, anti-corrosion and thermal barrier [2,10,11].

![Figure 2.2: Simplified sketch of a Plasma Spraying apparatus [2].](image-url)
The required high-temperatures are achieved by arranging for the carrier gas and coating powders to pass through an intense electric arc or an oxy-acetylene flame. The distinction between Plasma Spraying and Thermal Spraying regards the temperature reached by the available system: Plasma Spraying involves a work temperature sufficient to at least partially convert the mixture gas + powders to a plasma, while Thermal Spraying does not involve the plasma state but rather the livelihood of a flame as coating vehicle (the apparatus is nothing but an upgraded welding torch, supported by a powder feed system). Thermal Spraying needs a lower range of temperature than Plasma Spraying, that operates at high energy levels and high impingement speeds. Molten droplets disintegrate on contact instead of remaining as discrete: this process is known as splat formation, and the structure of the resulting coatings can be envisaged as a series of interlocking splats (Fig 2.3 (a)). Thus, structural defects are well distributed: oxides and voids inclusions constitute the major troubles of plasma coatings, because they determine its porosity and its tendency to crack propagation (Fig. 2.3 (b)). Indeed, also the strength of bonding at interface is critical to the performance of the coating [2].

![Figure 2.3](image-url): Plasma Sprayed coating. a) Simplified sketch of the mechanism of interlocking splats. b) Simplified sketch of the structure of the coating [2].
An interesting variant allows to remedy to the absence of effective plasma through the production of faster flames (up to 800 m/s): it is what is termed High Velocity Oxygen Fuel system (HVOF), that often improve the quality of adhesion due to the preponderance of mechanical interlock at interface. Other common variants (suitable for metal but incompatible with ceramics due to their low ductility) neglect the use of powders as coating material source (avoiding their costs and risks), replacing them with a wire-feed.

2.2.2 Vacuum-based coating methods: PVD and CVD

Vacuum-based coating methods involve a tuned vaporization of a coating source (a solid target or a gaseous precursor) gradually disintegrated to atomic species (ions, molecules or clusters) confined in a plasma state through physical transformations or chemical reactions. The former category groups all the Physical Vapour Deposition (PVD) methods, whose differ depending on the type of physical process that triggers the vaporization: heat supply (Evaporative Deposition, Electron Beam Assisted Deposition - EBAD, Ion Beam Assisted Deposition - IBAD), kinetic energy transfer (Sputtering Deposition, Pulsed Laser Deposition or Laser Ablation), electrical discharge (Arc Evaporation). The latter category collects all the Chemical Vapour Deposition (CVD) methods, whose differ depending to the type of chemical reaction often assisted by thermal or beam energy supply from which the coating material dissociates from a gas precursors, or synthesizes through the coupling of different gases [2,12].

Both PVD and CVD methods provide high-quality thin films: almost chemically “clean” and quite morpho-structurally homogeneous with no thermal damage to the substrate. However, PVD and CVD methods exhibit at least three order of common disadvantages. First of all, a good solid state adhesion is not always guarantee because of the low energy level of attaching metal vapour. The strategy of applying thinner bond-coatings at interface consisting of suitable interlayers is usually adopted in order to overcome this trouble. Second, the rate of deposition is so slow as to preclude the growth of coatings thicker than tens of microns for practical purposes. Finally, PVD and CVD are “line of sight” coating methods: the vapour (or plasma) tends to spread and fill the entire vacuum chamber and subsequently be deposited only on the exposed face of the item to be coated.
Sputtering deserved to be considered as the older and most common used PVD coating method based on the diffusion of removed atoms to produce a wide range of application: from reflective layers for optical mirrors, to metal-based anti-corrosion and anti-wear films to insulating protections for electronic chip. Its principle was discovered in the nineteenth century: a low pressure of inert gas (typically Argon) is maintained in the vacuum chamber, and it is ionized between two electrodes producing a gaseous plasma of high-energetic ions [12,13]. This gaseous plasma fills the chamber, dislodging atoms from both substrate to be coated (in order to clean and degrease it from surface contaminants) and target (the source of coating material). Reactive gases such as Nitrogen (for nitrides) or Methane (for carbides) can also be used to sputter compounds.

Figure 2.4: Simplified sketch a DC Magnetron Sputtering apparatus.

Electrodes voltage is usually governed by a Direct Current (DC), and in a more enhanced variant the plasma confinement is supplied by a Magnetron (Fig. 2.4): a circular ring-shaped magnet located between target and substrate. Its function is to trap electrons in order to prevent substrate overheating [2]. An integrated Moorfield® DC Magnetron Sputtering module (equipped with vacuum chamber and gages) has been adopted for the experimental campaigns will be described in chapter 4 (paragraph 4.2): see Fig. 2.5 and Tab 2.1 for details.


2.3 Surface texturing

The family of surface texturing collects all the manufacturing methods for the modification of surface topography, creating a uniform micro-relief with regularly shaped asperities or depressions with the aim of increasing the performances in various respects.

Some ideas in surface texturing have been emulated by observation of surfaces in nature, since it is very common to recognize naturally textured surfaces that optimize the adaptation to the environment of some species. A well known example is the patterned skin of some fish that might lead to reduction of drag forces during swimming. Nevertheless, the hierarchical micro-structure of lotus leave represents an element of huge interest due to its super-hydrophobicity. A greatest attention has recently received the texturing of gecko feet (Fig. 2.6), that allows a very strong adhesion force with a substrate so as to inspire the development of very strong adhesive devices employing a similar kind of texturing [14-16].

Table 2.1

<table>
<thead>
<tr>
<th></th>
<th>Moorfield\textsuperscript{®} - Minilab deposition system type S60A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pumps</td>
<td>Rotative, Turbo</td>
</tr>
<tr>
<td>Vacuum range</td>
<td>down to $10^6$ Torr</td>
</tr>
<tr>
<td>Gas lines</td>
<td>N\textsubscript{2}, Ar</td>
</tr>
<tr>
<td>Mass flow controllers</td>
<td>(0-50) sccm and (0-200) sccm</td>
</tr>
<tr>
<td>Sample heater</td>
<td>(0-800) °C</td>
</tr>
<tr>
<td>RF power supply</td>
<td>(0-300) W</td>
</tr>
<tr>
<td>DC power supply</td>
<td>(0-1200) W</td>
</tr>
</tbody>
</table>

Figure 2.5: Moorfield\textsuperscript{®} - Minilab deposition system type S60A and its principal characteristics (Table 2.1).
Figure 2.6: Gao et al. study [15] on the hierarchical adhesive structures of Gekko gecko. a): A toe of gecko contains hundreds of thousands of setae, and each seta contains hundreds of spatulae. b) and c): Scanning electron micrographs of rows of seta at different magnifications. d): Spatulae, the finest terminal branches of seta. ST: seta; SP: spatula; BR: branch.

Nowadays, surface texturing delineates a scientific and technological open-frontier where the area of micro-fabrication, well propelled by micro- and nano-electronics and high-advanced micro- and nano-mechanics, converge to surface science committed to study and demonstrate the various mechanisms of integrated micro-effects resulting in a macro-benefit that optimizes performance. Obviously, the design of surface texture is strictly correlated to the application, and thus the manufacturing method must be opportunely selected in order to satisfy the required cost-effectiveness and the texture parameters.

Surface texturing is proposed for a large number of applications, including: reduction of stiction in magnetic recording [17], increase of adhesion and mechanical interlocking [18], control of wettability [19], promotion of tissue ingrowth in biomedical prostheses [20], improvement of aesthetic appearance [21], control of drag forces in aero/hydro-dynamic application [22], increasing of friction and gripping action [23]. By the way, the widest used application of surface texturing regards the core of this thesis work, i.e. the optimization of tribological performances in terms of reduction of friction, damping of wear, and improvement of lubrication. This scientific challenge started in the 1960s, when Hamilton et al. [24] and Anno et al. [25] demonstrated the firsts evidences of the effect of surface irregularities on lubrication: they showed that regular distributions of micro-asperities could be adopted as an instrument for obtaining hydrodynamic operation in face seals. Since then, the correlation between lubrication regimes and surface topography has inspired a large number of studies.
Very few works have analyzed the performances of textured surfaces with nano-metric patterns [26,27] because such size range is considered very small and thus impractical for most tribological applications. So far, the majority of the studied cases deals with micro-metric patterns, characterized by features ranging from ten to few hundred micrometers wide, and few micrometers deep. Considering these scales, three main effects are expected to occur to improve the tribological performances of textured surfaces.

The first is the removal of wear debris, or better the entrapping of them inside the pockets that compose the texture, avoiding their presence between mating surfaces, which could cause friction instabilities and abrasive wear [28,29]. In this sense, a very comprehensive study was conducted by Becker and Ludema [30]: they developed a quite exhaustive qualitative empirical wear model that clarifies the crucial role of manufactured surface valleys filled by wear debris. Other related studies of Varenberg et al. [31] and Volchok et al. [32] illustrate a mechanism of fretting wear debris escape from the fretted zone into textured micro-pores (Fig. 2.7 (a)), that leads to the improvement of the fretting fatigue resistance and to the increase of the fretting fatigue life (Fig. 2.7 (b)) during cylinder-on-flat reciprocating test.

**Figure 2.7:** a) Varenberg et al. work [31]: Schematic description of pore filling mechanism. Filling starts from top (stage 1) towards center and bottom (stages 2 to 4). b) Volchok et al. work [32]: the beneficial effect of textured micro-pores (with different depth) on the mean fretting fatigue life during reciprocating test.
The second benefit is the supply of lubricant, or in other terms the oil-holding capacity to ensure a secondary source of fluid film for both stationary and moving contacts. Lots of experimental studies were carried out in order to compare the behaviours of smooth lubricated surfaces against textured ones covered by arrays of pockets of various shapes (dimples, grooves, squares, chevrons, ellipses, pyramids etc.) behaving as lubricant reservoirs.

An experimental pin-on-disk campaign carried out by Kovalchenko et al. [33] deserves a mention. They showed and explained beneficial effects of laser texturing on unidirectional sliding steel tested in starved lubrication conditions guaranteed by both high- and low- viscosity oils: the presence of micro-cavities was demonstrated to support the fluid film thickness so as to delay, or even inhibit the transition from mixed to boundary lubrication regimes (Fig. 2.8).

![Figure 2.8: Kovalchenko et al. work [33]: comparison of Stribeck curves related to pin-on-disk tests carried out on ground steel (disk 2: ■) polished steel (disk 1: ♦) and regularly laser-textured steel (disk 3: ▲). The presence of micro-cavities guarantees better tribological performances in starved lubrication conditions: no transition from mixed to boundary regime is observed.](image-url)
Another set of results gained from different ball-on-flat experimental campaigns by Pettersson and Jacobson [34] partially clarified the well debated role of size, shape, and orientation of micro-textures in terms of improving friction coefficient and wear rate under boundary lubrication regime. Micro-grooves and quadratic micro-pockets were studied as texture features. Especially their size and orientations with respect to the sliding orientation were demonstrated to influence the tribological behaviour (Fig. 2.9). The proposed explanations involve two phenomena: the concentration of local pressure instabilities at the edge of pattern features, and the frequencies with which the circle contact passed oil reservoirs. Enhancing the lubrication regime (from starved to full film) the effects of size and orientation expire: when an ample amount of oil was supply, the friction was rather insensitive to all configuration.

**Figure 2.9:** Pettersson and Jacobson work [34]. a) Summary of the performances of the textured surfaces in starved boundary lubricated sliding ball-on disk tests. The circles represent the elastic contact area related to each configuration. The micro-textures (grooves and squares) are of the three different widths: 5, 20 and 50µm. b) The friction coefficient as a function of number of cycles under starved boundary lubrication for surfaces with the pattern of 20 µm squares oriented along the sliding direction (□) and turned 30° from the sliding direction (■). c) The friction coefficient as a function of number of cycles under starved boundary lubrication for surfaces with the pattern of 20 µm wide grooves oriented perpendicular to the sliding direction (■) and parallel to the sliding direction (□).
The third effect due to surface texturing is the enhancement of hydrodynamic pressure between the surfaces due to the converging wedges constituted by the pocket. This effect has been analyzed via both numerical simulation and experimental investigation.

As mentioned above, the firsts evidences of surface irregularities acting as cavitation streamers on the hydrodynamic lubrication were described by Hamilton et al. [24] through visual observation of non-continuum lubricant films in optically flat transparent seals (1966). Based on these observation, the authors produced a simple analytical model to predict the effect of the geometry of micro-texture on the load support: they used Reynolds equation reduced to the two-dimensional form of the Laplace equation to describe the flow and they considered the pressure distribution by superposition of single-asperity solutions.

The main conclusion regards the optimum value of the number of asperities to maximize the load support: when the asperities are rarefied there is a little interaction between them, while as asperities become more closely packed the interaction increases so that the rate of increase of load support diminishes. The same considerations were extended to the effects of asperities radius and area fraction.

After exactly thirty years (1996), a similar study on mechanical seals allowed Etsion and Burstein [35] to develop a more refined mathematical model based on the concept of clearance, that is given by the balance between the closing force, obtained by a spring pressure, and the opening force, due to the hydrodynamic lift generated by the pattern features. Their approach corroborate the Hamilton’s results: even accordingly to experimental results [36] it is possible to predict optimum values for pocket size and surface coverage to maximize clearance.

A further model of Ronen et al. [37] allowed to predict also the optimum value for depth/diameter ratio of the pockets (Fig. 2.10 (a)) with good agreement with experimental results (Fig. 2.10 (b)) successively published by Ryk et al. [38].
In order to satisfy the needing of a widespread production of surface texturing applications, various manufacturing techniques has been developed and successively updated (mostly borrowed by the semiconductor industry). A tentative of database implementation oriented to the classification of possible texturing methods was recently carried out by H. L. Costa [39], who enumerates the techniques and their hypothetical practical applications, discussing about the requirements and the discriminations between processes.

By the way, in order to complete this chapter, a further detailed survey of surface texturing processes is redundant. Almost all of them are special declinations of the already treated surface finishing processes (see paragraph 2.2), exploiting the same basic principles aimed to the addition or removal of material as to produce regular matrices of micro-features in relief. Thus, the differences obviously regard the topographic selectiveness of such treatments by exploiting the interposition of custom devices that reproduce the designed pattern (i.e. masks, templates, stamps or moulds).
Texturing methods that involve adding material are mostly related to the deposition of patterned coatings by CVD or electroplating techniques [40,41]. Localized deposition is normally controlled by locally changing chemical or physical properties of the surfaces before the growth of the coatings through the pre-printing with inks or markers that can inhibit or favour the deposition process in order to generate a patterned relief. In the same way, methods that involve altering material such as patterned passivations or localized diffusions are exploited [42].

However, currently the majority of texturing methods involve removal of material. They rely on surface material erosion, or ejection, or moving of selected areas creating textures characterized by plateau and recessed sites, which can be continuous (grooves) or discontinuous and discrete (pockets or cavities). Selective removal of material can be achieved by three classes of strategies.

The first regards mechanical methods exploiting forms of localized grinding [43], embossing [44], vibrorolling [45], micro-cutting by sharp tips [26], shooting of hard and abrasive particles [46].

The second class of strategies regards forms of chemical etching, where active reagents are selectively applied to a surface in order to remove material in specific regions marked by a previous masking [47]. Electric current can be exploit to activate or assist chemical reactions in electrolytic cells [48]. Regarding this kind of approach, lithographic methods (photo-based or beam-based) are suitable for the pre-printing of the texture [49].

The third class of strategies is perhaps the widest used in both industry and laboratory research fields, and it involves the use of focused high-energetic beams (electrical discharge [50], ionic [27], laser [21,28,29;31-39;51-57]) as “direct writers”: pulses of sufficient energy to melt or vaporize a microscopic quantity of the surfaces generate each micro-feature whose size and shape are controlled by tuning the characteristic of the spot.
2.3.1 Laser Surface Texturing (LST)

Nowadays, photons are a very attractive tool in industry. As they have no charge, they do not repulse each other when they are confined into a very small space: this is a crucial peculiarity for micromachining. Thus, Laser Surface Texturing (LST) is one of the main texturing methods in Surface Engineering since more than fifteen years [21,28].

In lasers (light amplification by stimulated emission of radiation), stimulated emission occurs as a cascade because photons incident into matter stimulate electrons to transit from a higher level to a lower one emitting a photon that stimulates an atom to emit another photon with the same wavelength and phase.

Various media can achieve this goal. From their properties it follows the classification of the lasers whose differ in wavelength and thus also for their purposes of use: gaseous media (He-Ne, Ar, Kr, Xe, N₂, CO₂, or excimers such as ArF, KrF, XeCl and XeF), metallic vapours media (Cu, Au, HeCd, HeSe, HeHg), semiconductor media (the principal are: GaN- and GaAs-based) solid state media (the most used is Nd:YAG, largely adopted for micromachining).

When condensed phases are irradiated with laser pulses, massive molten material ejection is observed. This process is known as “ablation” [51,52]: the resolution depends on the wavelengths of the laser source used; the lateral dimensions of each singular ablated feature are linked to the incident spot size (depending on the optics of the system); the ablation rate depends on the energy density, and the final depth is determined by number of pulses and pulse duration (typically range from ms to fs).

These dependencies, and the role of principal irradiation conditions on micro-structuring, were deepened in an exhaustive experimental work carried out by Kononenko et al. [53] on laser textured TiN-coated substrates (Fig. 2.11).
Figure 2.11: Kononenko et al. work [53]. a) and b): Role of laser beam energy density on ablation rates measured for different wavelengths ($\lambda$) and pulse duration ($\tau$). $\lambda_{IR} = 1078$ nm: (a) $\tau_1 = 300$ ps, (b) $\tau_2 = 9$ ns; $\lambda_{visible} = 539$ nm: (a) $\tau_1 = 220$ ps, (b) $\tau_2 = 7$ ns; $\lambda_{UV} = 270$ nm: (a) $\tau_1 = 150$ ps, (b) $\tau_2 = 5$ ns. c): Dependencies of the micro-crater depth on the number of pulses at low energy density (1 J/cm$^2$) for different wavelengths and pulse duration ($\lambda_{IR} = 1078$ nm, $\tau_{IR} = 300$ ps; $\lambda_{visible} = 539$ nm, $\tau_{visible} = 220$ ps; $\lambda_{UV} = 270$ nm, $\tau_{IR} = 150$ ps).

When lasers are used to texture a metal surface, the ablation mechanism is localized by different techniques. The former and quite obsolete is the chopping of an unfocused laser beam through a rapidly rotating perforated disk that tunes the space between ablated micro-craters, and then focused to the surface [54]. Regarding this configuration (Fig. 2.12 (a)), the main advantage is in the fastness of processing, but the disadvantages are in the flexibility and accuracy. Typical micro-pockets diameters extend in the range of hundreds of micrometers [21], with almost irregular shapes because of the formation of lateral rims around the micro-pockets originated from ejected material. Indeed, a gas-assist apparatus is even necessary to guide the flow of molten material away from the edges of pockets and to prevent oxidation of the freshly melted metal [55].

Another possible configuration involve the use of a patterned mask (Fig. 2.12 (b)) through which is projected a large cross-section of laser beam [56]. This kind of approach guarantees a major flexibility to produce variously shaped micro-features and a minor processing time, but the cost-effectiveness is in some cases prohibitive due to the mask manufacturing.
Figure 2.12: Different approaches for laser texturing. 

a) Pawelski et al. [54] experimental layout: chopping of an unfocused laser beam through a rapidly rotating perforated disk. 

b) Mailis et al. [56] experimental layout: use of patterned mask through which is projected a large cross section of an excimer laser beam. 

c) Vincent et al. [57] experimental layout: direct driving of the laser beam towards the sample.
A convenient compromise is the strategy involving a CNC-system (Computer Numerical Control) and a galvanometric scanner [57] to drive the laser beam over a designed array of regularly spaced region of the surface generating the texture (Fig. 2.12 (c)).

This approach allows high accuracy (pocket diameters as small as few microns could be machined [39]) because it exploits the use of focused laser beam of very short pulse duration (typically faster than hundreds of ns) to promote localized ablation.

The main drawback is that each pocket is machined individually, thus making the process very time-consuming: the shorter is the pulse duration (down to fs), the higher is the aspect-ratio of the micro-features, but the longer becomes the processing time. On the other hand, the increase of the pulse duration leads to breakdown the processing time but it also results in the diffusion of relatively large Heat Affected Zone (HAZ) in proximity of the border of the micro-feature. The HAZ thickness is roughly a maximum among the radiation absorption length ($L_{opt}$):

$$L_{opt} = \frac{1}{\alpha}$$  \hspace{1cm} (2.1)

and thermal diffusivity length ($L_{th}$):

$$L_{th} \approx \sqrt{\tau \chi}$$  \hspace{1cm} (2.2)

where $\alpha$ is the optical absorption coefficient, $\chi$ is the thermal diffusivity and $\tau$ is the pulse duration [53]. These latest aspects will be discussed in detail in chapter 5.
2.4 References

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Chapter 2 - Surface Engineering: a brief survey of techniques


Chapter 3

Cross-section analysis and tribological characterization of innovative coatings

3.1 Dual Beam applications and strategies of use

The Dual Beam FEI Strata™ DB 235 system (Fig. 3.1) is a “state-of-the-art” tool for micro- and nano-imaging and machining characterized by a high degree of versatility combining a Focused Ion Beam (FIB) with a Secondary Electron Microscope (SEM) co-focally installed at 52° from each other into a vacuum chamber equipped with a set of detectors and a Gas Injection System (GIS). Both columns are oriented towards a movable sample stage (able to tilt between -5° and +57°), and can be scanned (even contemporarily) to analyze surfaces in great detail over a wide range of magnification detecting signals (secondary or backscattered) generated upon interaction with primary beam particles (ions or electrons). Moreover, the columns can be exploited for local patterning by both “top-down” and “bottom-up” strategies to create micro-features in relief.

Figure 3.1: a) Dual Beam FEI Strata™ DB 235 system. b) Schematic description of SEM and FIB columns. c) Schematic representation of Dual Beam configuration: electron and ion columns are co-focally installed (52° tilt angle).

SEM column is equipped with a Schottky Field Emission Gun (SFEG) electron source, and is designed to work with low accelerating potential and high magnification. The energy beam is tunable between 1 KeV and 30 KeV. A combination of scan coils and objective lenses allows to deflect the beam in a scanning pattern focusing the spot to illuminate the sample surface at High Resolution (HR). Indeed, when even the immersion lens is switched on, a magnetic field wraps the...
scanned sample area enhancing the number of secondary electrons collected by the detectors, so that a Ultra High Resolution (UHR) mode is able to guarantee analytical operation at magnification greater than 1000-2000 X.

FIB consists in an ion column instrumented by an ion source and optical sections constituted by apertures and electrostatic and magnetic lenses which focus the beam and deflect it to selected areas on the target. The Ga⁺ Liquid Metal Ion Source (LMIS) is essentially a “point source” (the apex extends for few nanometers) that provides a very high brightness and a high angular intensity. It consists in a liquid gallium reservoir and a conical shaped field emitter needle to which the liquid is pulled as to form the so-called “Taylor cone”, namely the best condition for ion emitting [1]. This condition is reached applying an opportune electric field of sufficient strength (E) so as to respect the balance of surface tension (γ) and electrostatic forces dictated by:

\[
\frac{1}{2} \varepsilon_0 E^2 = \frac{2 \gamma}{r}
\]  

(3.1)

where \(\varepsilon_0\) is the permittivity of the vacuum, and \(r\) the principal radius cone [2]. Once generated, the monochromatic ion beam (\(E_{ion} = 30\)KeV) is extracted and projected through a combination of lenses and apertures to minimize spherical and chromatic aberrations, or to divert the beam away from the stage and into a Faraday cup in order to preserve the sample from an unwanted exposure (Beam Blanking Assembly). The automatic control of the apertures allows to tune and switch the size (diameter ranging from few nanometers to few microns) and the current of the beam (ranging from few picoAmperes to several tens of nanoAmperes).

Several processes occur during the interaction between an ion beam and a solid (Fig. 3.2). Ion-solid interactions and their range are substantially different than electron-solid interactions because of the masses of striking particles. Impinging ions are less penetrative than electrons, but can cause the displacement of target atoms activating a number of phenomena which can be usefully exploited in making, breaking and altering structures on an extremely small scale. Both elastic and inelastic processes develop with different probability during ion-matter interactions. Inelastic processes result in the emission of other form of energy such as X-rays, optical photons and secondary electrons (or other atomic species). Due to their copious generation and ease in detection, secondary electrons represent by far the most exploited signals for surface mapping.
Figure 3.2: Schematic representations of possible ion-matter interactions [3].

SEM and FIB imaging principles differ since incident electrons generate only secondary electrons, while incident ions produce both secondary electrons and ions. FIB images achieved by Scanning Ion Microscopy (SIM) and SEM images differentiate because of contrast mechanisms and scanning features. While electron beam is not destructive, when the ion beam is focused over a sample, it partially modifies the surface by erosion at a rate determined by the incident beam current and sputter yield of the sample material, limiting the time that it may be imaged. But apart from this disadvantages, SIM is complementary to SEM because of two main reasons.

The first is due to the higher sensitivity to surface topography, motivated by the production of low-energy secondary electrons which cannot escape from deep below the surface.

The second reason is related to the “channelling effect” (Fig. 3.3) and the correlated higher sensitivity to the crystalline structure of the sample: during interaction with crystalline or polycrystalline materials, the primary ions encounter privileged orientations of rows of atoms along which they could travel deeper into the solid producing an image contrast that gives informations about the size and shape of grains and crystalline domains [1]. Regarding this approach, an application will be described in chapter 5.
Among elastic ion-matter interactions, the most exploited is physical sputtering governed by the momentum transfer from incident ions to surface atoms: FIB could be used as a miniature milling machine for shape modification of the target, or as a lathe to remove selected areas digging with great precision. A more complex process is chemical sputtering, that occurs in presence of reactive gases as chemical reaction are activated by the incident ions decomposing the precursors and forming new layer compounds above the rastered target. Thus, FIB could be exploited as a “local CVD-assistant” in order to grow highly resolved micro-features. The availability of these two just mentioned approaches at small scales - “top-down” ion milling, and “bottom-up” IBID (Ion Beam Electron Deposition) - justifies the exclusive and versatile capability of “micro-machining” [1-3]. In this sense, FIB is employed for various applications: patterning via fabrication of micrometric or sub-micrometric structures in relief [4-6]; manufacturing, refinement, reshaping or repairing of micro-components and devices [3,7]; preparation of lamellas for Transmission Electron Microscopy (TEM) analysis [8]; sub-surface diagnostics [9-11].

In particular, it is possible to make a local “micro-cross section” of the sample in order to reveal its morphological and structural depth profile by milling trench of surfaces trough progressive rastering step. The discovered wall could be prevented against relevant additional ion-induced damage trough a thin shield (typically Pt- or W-based) grown in situ by IBID, and finally imaged by both SEM and FIB tilting the sample stage. This latest strategy is useful for failure analysis, and gives major opportunities in tribological and mechanical investigations about deep cracking, buried defects distributions, coating interface behaviours, grain structure of material
surfaces [9-11]. In a mentionable work [11], Shakhvorostov et al. investigated about the consequences of the exchange of heat and mechanical intermixing during tribological interaction (pin-on-disk tests). By means of FIB “micro-cross section” analysis (Fig. 3.4), they identified a sub-surface modified “tribo-layer” (few hundred nanometers thick) characterized by a gradual formation of nano-crystalline grains: this structural transition is ascribable to the energy input due to tribological stressing.

In summary, Dual Beam machine guarantees two major experimental approaches: imaging and micro-machining. For these reasons it could be meant as a huge opportunity for tribology, and it inspired most of the research activities carried out by the author during Ph.D..

In this chapter, highlights of two papers related to FIB-based sub-surface characterizations are reported. The first (Material Letters, 2008) deals on instrumented sharp indentation, a technique often employed for micro-mechanical investigation. To verify the possible influence of sub-surface cracking and material anisotropy, Vickers indentations on plasma-sprayed TiO₂ were “micro-sectioned” by FIB. The second (Journal of Thermal Spray Technology, 2009: in press) reports about a tribological characterization carried out on promising “Duplex” systems (thin DLC films grown onto thick intermediate hard coatings). The integration of ball-on-disk campaigns with successive Dual Beam “micro-cross section” analysis allows to correlate the tribological behaviours to sub-surface microstructures.

Figure 3.4: Shakhvorostov et al. work [11]. a) Top view: FIB “micro-cross section” milled between points A and B (see the depth profile in the relative sketch). A W-shield was grown to prevent the topmost material from mechanical intermixing upon contact with the ions. b) Cross-sectional view of the discovered layer.
3.2 TiO$_2$ plasma-sprayed coating: a FIB study

Sharp indentation testing is commonly employed to characterize important material properties, like hardness, fracture toughness, elastic modulus, thanks to the simple experimental set-up, small sample size and near-non-destructiveness [12]. Particularly, it is often used to characterize thermally-sprayed ceramic coatings [13], whose tribological behaviour is significantly correlated to the above-mentioned properties [14].

Crucial to Indentation Fracture Toughness (IFT) measurement is the ability to produce suitable radial cracks that arise at the vertexes of Vickers indentation marks. While established results exists on bulk ceramics, difficulties arise for thermally-sprayed ones. Not only thermally-sprayed ceramics are orthotropic (i.e. with perpendicular symmetry axis), but, most importantly, interlamellar boundaries, pores, defects, and complex intrinsic intralamellar stresses cause anomalous cracking [13,15]. Irregular propagation paths of radial cracks [16] and occurrence of other kind of cracks impair toughness quantification. Thus, ad-hoc modifications to the method have sometimes been necessary [17], and IFT computation for thermal-spray ceramics has been criticized [15]. Hardness and elastic modulus values have also been found to be affected by size effects, depending on pores, defects and cracking phenomena [18,19].

Thus, an investigation of thermal-spray ceramics cracking behaviour is necessary: by sectioning indentations using the Focused Ion Beam (FIB), sub-surface cracking can be characterized. FIB has been very rarely adopted for thermal-spray coatings [16], but examples of indentation cracking investigation are now being issued [10].

TiO$_2$ powders (Sulzer-Metco SM102) were atmospheric-plasma-sprayed (Sulzer-Metco F4-MB torch) on grit-blasted C40 steel plates. Depth-sensing Vickers micro-indentations (Micro-Combi Tester, CSM Instruments) were performed at 1 N load (0.8 N/min loading/unloading speed, 15 s loading time) and at 5 N load (4 N/min loading/unloading speed, 15 s loading time). Hardness and elastic modulus were obtained by the Oliver–Pharr procedure [12] (Poisson’s ratio assumed to be 0.23). Indentations on the top surface and “macro-cross section” of the samples were sectioned and observed using the Dual Beam Machine. FIB “micro-cross sections” were produced using a 20 nA ion beam current for 5 N-load indentations and a 7 nA ion beam current for 1 N-load ones, and subsequently polished using a 1 nA ion beam current for 5 N-load indentations and 300 pA for 1 N-load ones. The “micro-sectioned” surface was then observed using the SEM column.
Small rounded pores and transverse microcracking (perpendicular to the substrate interface), from splat quenching, are detectable (Fig. 3.5 (a)); FIB sectioning highlights a detail of a transverse microcrack (Fig. 3.5 (b), arrow). The overall porosity is (9±1)%, pore roundness is 0.53±0.02, and, among pores with roundness <0.40, those having a major axis inclined by more than 45° respect to the substrate interface direction are (58±2)%, suggesting that transverse microcracks are prevailing upon interlamellar defects: this indicates good in-flight particle melting and interlamellar cohesion [20].

**Figure 3.5:** SEM images. a) “Macro-cross section” of TiO₂ coating. b) FIB “micro-cross section” on TiO₂ coating top surface: black arrow indicates a transverse microcrack.

Remarkably, indentation load significantly affect hardness and elastic modulus values measured on “macro-cross sections” but not those measured on polished top surfaces (table 3.1).

<table>
<thead>
<tr>
<th>Indenter configuration</th>
<th>Vickers 1N load</th>
<th>Vickers 5N load</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness [GPa] - Top surface</td>
<td>8.0 ± 1.5</td>
<td>7.6 ± 0.4</td>
</tr>
<tr>
<td>Hardness [GPa] – “Macro-Cross section”</td>
<td>10.3 ± 1.1</td>
<td>8.5 ± 0.6</td>
</tr>
<tr>
<td>Elastic Modulus [GPa] - Top surface</td>
<td>190 ± 20</td>
<td>195 ± 15</td>
</tr>
<tr>
<td>Elastic Modulus [GPa] - “Macro-Cross section”</td>
<td>182 ± 11</td>
<td>129 ± 5</td>
</tr>
</tbody>
</table>

**Table 3.1:** Depth-sensing microindentation test results.

Also, FIB “micro-cross sections” reveal much different cracking phenomena in top surface and “macro-cross section” indentations. Indeed, although 1 N-load Vickers indentations on coating “macro-cross section” display limited radial cracking (Fig. 3.6 (a), arrows), FIB “micro-cross sections” (Fig. 3.6 (b)) reveal significant sub-surface cracking. Since these cracks are much more numerous than on untested material (Fig. 3.5 (b)), they are obviously a consequence of indentation. Moreover, previous studies demonstrated that FIB ion milling technique does not introduce relevant
additional damage to the microstructure [10]. The cracks propagation paths seem irregular, consistently with the existence of potential cracks deflection mechanisms: multi-phase structure, unmelted particles, co-existence of stronger and weaker interlamellar boundaries [13], different quenching stress in nearby splats [21], etc. However, cracks close to the indentation surface seem to propagate mainly in the direction parallel to the surface itself (Fig. 3.6 (b), label 1), while deeper they mainly propagate perpendicularly to it (Fig. 3.6 (b), label 2). Former numerical stress distribution analyses of sharp indentation [12,22] indicate that, immediately below the indenter, a region of very severe plastic shearing exists: probably, severe shear stresses are producing cracks in this region. In the underlying elastoplastic region, cracks likely propagate perpendicularly to the highest principal stress direction. Near the surface, close to the indentation corners, the radial crack trigger point is detectable (Fig. 3.6 (b), circle), clearly suggesting that radial cracks are not half-penny type (i.e. semicircular cracks extending all across the indentation mark) [23].

Figure 3.6: SEM images: 1 N-load Vickers indentation on TiO₂ coating “macro-cross section”. a) Top view: black arrows indicate radial cracking. b) FIB “micro-cross section” of the former indentation: sub-surface cracks (label 1) close to the indentation surface, and deeper cracks (label 2) are visible. The radial crack trigger point is detectable (white circle).

At 5 N load, radial cracking is enhanced and much damage exists along the indentation sides (Fig. 3.7 (a)). Even more severe sub-surface cracking has occurred (Fig. 3.7 (b), label 1). Only at the very bottom of the FIB “micro-cross section”, cracks do propagate perpendicular to the sample surface (Fig. 3.7 (b), label 2). Probably, the volume of the severe plastic shearing region is enlarged, because stresses are being increasingly redistributed from the area under the indenter to nearby regions. Radial cracks, when micro-sectioned by FIB, also display very irregular propagation behaviour, with deflection and branching phenomena (Fig. 3.7 (c)).
Doubts on the reliability of material properties measured by Vickers indentation on thermal-spray coatings cross-section arise out of these findings. Sub-surface cracks formed during indentation can largely contribute to the observed hardness and modulus decrease, particularly at high loads [18]. IFT is assessed by measuring radial cracks produced by Vickers indentation.

The numerous proposed models (thoroughly reviewed in [23]), relying upon fracture mechanics analyses of radial crack propagation, are ultimately based on the balance between the work of indentation and the crack propagation energy. If cracks different from the radial ones exist, as in the present case, their basic assumptions are invalidated. Furthermore, radial cracks themselves have irregular sub-surface propagation, not accounted for by the models.

Differently from indentations on “macro-cross sections”, Vickers indentations on the top surface display much less material uplift (Fig. 3.8 (a)) and, most importantly, almost no sub-surface cracking both at 1 N load (Fig. 3.8 (b)) and at 5 N load (Fig. 3.8 (c)). Since, in this case, no newly-formed sub-surface cracks will interfere with loading/unloading behaviour, the hardness and elastic modulus values measured at both indentation loads are very similar.
In summary:

- Dual Beam investigation shows remarkable sub-surface cracking under sharp indentations on the “macro-cross section” of plasma-sprayed TiO$_2$, even at relatively low loads. Cracking becomes more relevant as the load increases, affecting the indentation response (hardness, elastic modulus).

- The very irregular cracking behaviour casts doubts on the quantitative reliability of IFT measurement. The much different cracking behaviour of cross-section and top surface indentations also indicates significant anisotropy in material strength: it is apparently much higher when loading in the transverse direction.

- This preliminary work highlights the need for further accurate investigations of sub-surface cracking behaviour during sharp indentation.
3.3 Tribological and sub-surface characterizations of “Duplex” systems

Diamond-Like Carbon (DLC) films generally combine high hardness and low-friction behaviour. They are therefore extremely appealing for several industrial applications, e.g. protection of plastic injection moulds, coating of automobile parts and of components for industrial plants. In those applications, DLC films deposited onto steel substrates can indeed reduce significantly the coated component’s wear rate and, most importantly, the friction coefficient [24-26].

However, DLC films are intrinsically brittle and their thickness is limited to <5 µm by various factors, including the generally low deposition rates of PVD and CVD techniques and the high levels of residual stresses in the deposited film [24].

Due to their low thickness, DLC films cannot entirely carry the stress distribution generated by the contact between the coated component and its counterpart: when the stress in the substrate exceeds its yield strength, the coating is dramatically overloaded [27] and it can crack and/or delaminate [28,29].

In order to overcome these problems, a thick (>100 µm) interlayer having high hardness and modulus can be interposed between the DLC coating and a soft substrate (like a carbon steel). The contact stress distribution would indeed be borne by the hard interlayer, thus avoiding the troubles connected to the low yield strength of the substrate. “Duplex” systems, where DLC films or other hard thin-film coatings (like TiN) are deposited onto thick interlayers, have seldom been dealt with in the literature, although very promising results have been put forward [30-32].

A tribological characterization integrated with a successive sub-surface FIB study is aimed to verify the improvements which the use of thick interlayers can produce in the adhesion and wear behaviour of DLC-based thin films, deposited onto carbon steel substrates by hybrid PVD-CVD technique.

Fig. 3.9 shows a simplified layout of the tested system, constituted by three units. From the bottom to the top: a steel plate as substrate (grit-blasted C40 steel: Ra ≈ 0.02 μm), a thermally-sprayed (TS) thick interlayer, and a three-layered DLC-based thin film.
Different TS cermets were tested as interlayers for DLC-based thin films, in order to compare the provided benefit. Specifically:

- atmospheric plasma-sprayed (APS, Sulzer-Metco F4-MB plasma torch) Ni – 50wt.% Cr (powder: Sulzer-Metco Amdry 350C), with a final Ra $\approx 0.1 \mu m$ (after successive polishing steps);

- atmospheric plasma-sprayed (APS, Sulzer-Metco F4-MB plasma torch) Al$_2$O$_3$ – 13wt.% TiO$_2$ (powder: Sulzer-Metco 130) having a NiCoCrAlY bond coat (powder: Sulzer-Metco 461NS) in order to improve its adhesion, with a final Ra $\approx 0.1 \mu m$ (after successive polishing steps);

- High Velocity Oxigen Fuel-sprayed (HVOF, Praxair-Tafa JP5000 torch) WC – 17wt.% Co (powder: Tafa 1343), with a final Ra $\approx 0.03 \mu m$ (after successive polishing steps).

were considered, because they are representative of the three main categories of materials which are commonly employed in the thermal spray industry, namely metallic alloys, oxide ceramics and cermets [33-35]. The thickness of all intermediate coatings is larger than 200 $\mu m$.

The three-layered DLC-based thin films were deposited both on the bare C40 substrate, and on the three thermally-sprayed interlayers for comparison. The three-layered DLC-based thin film
was manufactured in a hybrid PVD-CVD coating system, equipped both with magnetron sputtering (MS) sources and with electron cyclotron resonance chemical vapour deposition (ECR-CVD). A thin (0.5 μm thick) Cr adhesive layer was deposited by magnetron sputtering. A further WC/C buffer layer (1.5 μm thick) was also deposited by magnetron sputtering, in order to mitigate the steep change between the hardness of the underlying surface and that of the DLC top layer. A 2.5 μm thick DLC top layer was then produced by ECR-CVD (gaseous precursor: C₂H₂).

Unidirectional ball-on-disk tribological tests were performed in dry conditions on thin film-coated samples. Sintered alumina balls (3 mm diameter, nominal hardness HV = 19 GPa) were employed as counterparts. Tests were performed at room conditions (temperature (21±2) °C, relative humidity (55±2)%) and at 300 °C, using a normal load of 10 N, a sliding speed of 30 cm/s and a total sliding distance of 5000 m.

The wear rates of the samples were determined by optical confocal profilometry (Conscan Profilometer, CSM Instruments), the wear rates of the pins were determined by measuring the diameter of the worn cap using an optical microscope.

The wear scars on the coated samples were also observed and micro-sectioned by using the Dual Beam Machine. “Micro-cross sections” were produced by FIB using a 5 nA ion beam current and polished using a 300 pA ion beam current. A Pt-layer was previously applied in order to protect the surface of the sample, assisting the local deposition by FIB (300 pA ion current). The “micro-sectioned” surface was then observed using the SEM column.

Neither along the interface between the thin-film coatings and the polished thermally-sprayed interlayers, nor along the thin film-C40 interface can large defects be noted (Fig. 3.10). The three layers composing the films, namely DLC, WC/C and Cr, are clearly recognizable in the FIB-produced “micro- cross sections” and show sharp interfaces.
Figure 3.10: SEM images of FIB “micro-cross section”. a) Three-layered DLC-based film deposited on the bare C40 substrate. b) Three-layered DLC-based film deposited on the HVOF-sprayed WC-17%Co interlayer. The circle indicates defects in the MS layers, due to imperfections on the polished WC-Co surface.

On the very smooth surface of the polished C40 steel, the multi-layer thin film can grow free of any apparent defect (Fig. 3.10 (a)). By contrast, small imperfections exist on the polished surfaces of the thermally sprayed interlayers, because of features like lamellae boundaries, or WC particles standing out of the Co metal matrix in the cermet coating (Fig. 3.10 (b)). These small imperfections induce defects in the sputtered Cr-adhesive and WC/C-buffer layers (Fig. 3.10 (b), circle), but such defects do not extend to the DLC layer. The smooth DLC top layer can therefore preserve the very low roughness of the polished C40 and HVOF-sprayed WC-Co surfaces (Table 3.2).

<table>
<thead>
<tr>
<th></th>
<th>DLC on C40</th>
<th>DLC on WC-Co</th>
<th>DLC on Al₂O₃-TiO₂</th>
<th>DLC on NiCr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra (μm)</td>
<td>0.030</td>
<td>0.040</td>
<td>0.183</td>
<td>0.157</td>
</tr>
</tbody>
</table>

Table 3.2: Average roughness (Ra) of the DLC-based thin films deposited onto the various polished surfaces.

The roughness of the polished APS surfaces (NiCr and Al₂O₃-TiO₂) is larger by one order of magnitude because of small imperfections like lamellae boundaries or oxide inclusions and unavoidable porosity [36,37], due to the intrinsic characteristics of the deposition technique [34]. After surface polishing, open porosity is therefore present on the surface of APS coatings: the DLC-
based film is clearly too thin to fill in and cover these open pores completely (Fig. 3.11 (a)), although it can be found inside some of them (Fig. 3.11 (b)).

![Image of SEM images of the DLC-based thin film deposited on the APS-Ni-50%Cr interlayer.](image)

**Figure 3.11:** SEM images of the DLC-based thin film deposited on the APS-Ni-50%Cr interlayer. a) Top surface: black circle indicates an open pore. b) FIB “micro-cross section” produced in correspondence of an open pore: DLC-based film is too thin to fill pores, but traces of the three-layer are present inside them.

### 3.3.1 Room temperature tests

The evolution of the friction coefficient during the dry sliding ball-on-disk test performed at room temperature immediately indicates that the DLC-based thin film deposited on the Al₂O₃-TiO₂ interlayer is completely removed soon after the beginning of the wear test (Fig. 3.12 (a)) and, accordingly, the final wear rate of both the coating and the counterpart is larger by several orders of magnitude than in all other cases (Fig. 3.12 (b)).

![Image of friction coefficient and wear rate evolutions.](image)

**Figure 3.12:** Ball-on-disk test performed at room temperature. a) Friction coefficient evolutions. b) Wear rates of coatings and static counterparts.
The FIB “micro-cross section” obtained in correspondence of the brittle failure area shown in Fig. 3.13 (a), reveals that, under a thin layer of wear debris, the Al₂O₃-TiO₂ ceramic is severely microcracked (Fig. 3.13 (b), circle). This observation supports the hypothesis that delamination is not caused by failure in the thin film or at the interface, but inside the ceramic layer.

**Figure 3.13:** SEM images: wear scar produced after 500 m sliding at room temperature on the DLC/Al₂O₃-TiO₂ system. 
(a) Top surface: spallation due to brittle failure of the ceramic interlayer is visible. The black rectangle indicates the area subsequently micro-sectioned by FIB. 
(b) FIB “micro-cross section”: DLC-based film is completely delaminated. The black circle indicates the microcracked interface of the ceramic interlayer capped by wear debris.

By contrast, the DLC-based film deposited onto the WC-Co interlayer has not undergone any cracking or spalling during the whole sliding test at room temperature. The DLC top layer has simply undergone mild polishing wear (Fig. 3.14 (a)), which is typical of DLC films when their substrate does not yield [30,38].

The WC-Co interlayer indeed possesses very high hardness, capable of providing excellent support to the hard and brittle top layer (Fig. 3.14 (b)). Under these conditions, DLC film can express its tribological qualities at best (recall Fig. 3.12).
Chapter 3 - Cross-section analysis and tribological characterization of innovative coatings

Figure 3.14: SEM images: wear scar produced after 5000 m sliding at room temperature on the DLC/WC-Co system. 

a) Top surface: a rather mild abrasion of the DLC top layer is appreciable. 
b) FIB “micro-cross section” produced inside the wear scar: the three-layered DLC-based film is almost intact. Below, the ceramic interlayer does not show any tribologically-induced defects.

The DLC-based thin films on the bare C40 substrate (Fig. 3.15 (a)) and on the NiCr interlayer (Fig. 3.15 (b)) exhibit microcracking and localized spallation, phenomena which are known to occur when the substrate yields under the applied contact pressure. Previous literature [28] indicates that such wear mechanism is characteristic of a “borderline” situation: if contact conditions become only slightly more severe, complete delamination of the DLC-based film occurs. Due to this local spallation, the wear rates of the coated sample and of the ball are larger than in the case of the WC-Co interlayer (recall Fig. 3.12 (b)).

Figure 3.15: SEM images: wear scar produced after 5000 m sliding at room temperature on the DLC/C40 system (a) and DLC/NiCr system (b). Both top surfaces exhibit microcracking and local spallation.
3.3.2 High temperature tests

Increasing the temperature to 300 °C reduces the hardness and the load carrying capacity of the C40 steel substrate and of the NiCr interlayer; as expected, contact conditions become more severe and complete delamination of the DLC-based thin film occurs well before the end of the 5000 m-long tribological test (Fig. 3.16). On the contrary, the interpretation of the behaviour of the films deposited on the WC-Co and on the Al₂O₃-TiO₂ interlayers is less straightforward. The performance of these two layers is indeed reversed: the film on the Al₂O₃-TiO₂ substrate never delaminates completely, and retains a quite stable friction coefficient, whereas the film on the WC-Co interlayer comes to a complete delamination, even tough after a much longer sliding distance than the films on C40 and on NiCr.

Sub-surface microstructures related to Al₂O₃-TiO₂ and WC-Co interlayers were observed to change at high temperature. FIB “micro-cross sections” obtained in correspondence of the wear scar of the film on the Al₂O₃-TiO₂ interlayer at the end of the 5000 m-long sliding test, reveal that cracking of the interlayer is significantly reduced (compare Fig. 3.17 (a) to Fig. 3.13 (b)), so that spallation due to failure of the ceramic interlayer is largely prevented.

It would therefore seem that the toughness of the ceramic interlayer increases with increasing temperature [39], whereas its hardness is not remarkably impaired. Contrarily, FIB “micro-cross sections” obtained in correspondence of the wear groove of the film on the WC-Co interlayer after a sliding distance of 2000 m (i.e. slightly before the delamination of the DLC film),
a remarkable alteration in the WC-Co layer’s microstructure is apparent (compare Fig. 3.17 (b) to Fig. 3.10 (b), and to Fig. 3.14 (b)).

Specifically, it seems that the carbide grains have been fractured and comminuted (Fig. 3.17 (b), circle). It might be speculated that, at 300 °C, the hardness of the Co matrix definitely decreases; therefore, the metal matrix yields and most of the contact stresses are distributed on the WC particles, which become overloaded and undergo brittle fracture. The plastic flow of the metal matrix subsequently embeds the comminuted carbide fragments.

Figure 3.17: SEM images of the FIB “micro-cross sections” of the wear scars produced at 300 °C. a) DLC/Al₂O₃-TiO₂ system after 5000 m sliding distance: the three-layered DLC-based film is almost preserved. b) DLC/WC-Co system after 2000 m sliding distance: DLC top layer is completely delaminated. Below, the black circle indicates microstructural alterations in the WC-Co layer.
In summary:

- By using a combined magnetron sputtering (MS) – electron cyclotron resonance chemical vapour deposition (ECR-CVD) technique, three-layered DLC-based thin film (consisting of a magnetron sputtered Cr-adhesive layer, a magnetron sputtered WC/C-buffer layer and a DLC-top layer) were deposited onto bare C40 substrates, and onto various polished thermally-sprayed interlayers (namely: Ni-50%Cr, Al₂O₃-13%TiO₂ and WC-17%Co). This group of promising “Duplex” systems was characterized through intensive ball-on-disk campaigns, integrated by Dual Beam “micro-cross section” investigations which allowed to correlate the tribological behaviours to sub-surface microstructures.

- The tribological properties of the three-layered DLC-based film mainly depend on the properties of the interlayer. The results indicate that the hardness of the interlayer is of primary importance: a relatively soft interlayer, like the NiCr one, does not improve the sliding wear behaviour of the DLC-based film. However, the toughness of the interlayer is also very important: at room temperature, the hard but very brittle Al₂O₃-TiO₂ interlayer fails under severe contact conditions, thus leading to complete removal of the film. Consequently, at room temperature, the hard and tough WC-Co cermet interlayer offers the best performance; indeed, it succeeds in preventing any cracking and spallation phenomena in the thin film.

- At 300 °C, the presence of a hard interlayer is even more important, because the load-carrying capability of the steel substrate is further impaired, so that full delamination of the coating soon occurs. Contrarily to the room temperature conditions, the best performing interlayer at 300 °C is the Al₂O₃-TiO₂ one; indeed, brittle fracture of the interlayer seems largely reduced. By contrast, the WC-Co interlayer suffers a microstructural alteration, because of the combined effect of the severe contact stress and of the high temperature. Therefore, it partly loses its load-carrying ability and it cannot prevent the delamination of the film.
3.4 References


Davis JR, *Handbook of Thermal Spray Technology*. ASM Int. (2004);


Chapter 4

Tribological behaviour of laser surface textured steel

This chapter reports a recently published study (Wear, 2008) on the effects of surface modification by Laser Surface Texturing (LST) on tribological performances of nitriding steel suitable for automotive applications: the aim of the work regards the experimental investigation of the effects of micro-dimpling, by studying the tribological behaviour of mating contact surfaces working in different lubrication regimes.

The further paragraph highlights the preliminary results (La Metallurgia Italiana, 2009: in press) concerning a tribological characterization of a combined application of LST and PVD hard thin coating (CrN) on steel.

4.1 30NiCrMo12 textured steel: pin/ball-on-disk campaign

In a reciprocating internal combustion engine, thermal and mechanical efficiencies are relatively low, since much of the fuel energy dissipates as heat loss and friction. The major portion (48%) of the energy consumption developed in an engine is due to friction loss. Looking to the entire friction loss portion, engine friction loss is 41%, while only a rough 7% is ascribed to transmissions and gears [1].

Sliding of piston inside liner and rotating engine bearings mostly contribute to friction dissipation. Different automotive components rely on different lubrication regime during a single cycle. Some of these like journal and thrust bearings are designed to operate in the hydrodynamic lubrication regime, whereas others like piston-rings that slide inside liners are developed to perform in mixed or boundary lubrication (in isolated cases even in absence of lubricant). Metal-to-metal contact is expected to take place only at low speed and high loads for the first ones, while surface contact occurs for the second ones: in this last case is necessary to protect surfaces in order to avoid failure of the engine. Also for metal-to-metal contact, in particular for journal and thrust bearing, buffer material like bronze are widely used to improve wear resistance and decrease friction [2]. The efficiency, reliability, and durability of such components depend on the friction that occurs at a sliding contact interface.
Surface hardness and chemical composition play a dominant role against wear of materials under sliding conditions. Many engineering components made of ferrous materials are nitrided to improve wear, corrosion and fatigue strength. Diffusion of nitrogen on steel surface results in the formation of compound layer and diffusion layer, and improves the sliding wear behaviour [3]. In addition, both the need to reduce friction, and the desire to increase the load capacity or the power density of engine elements, require effective lubrication strategy for sliding surfaces [4].

Within this contest, a huge interest is focused towards innovative surface treatments that were recently developed in order to improve mechanical and tribological performances of metal engine components [5,6]. As already explained in chapter 2 (see paragraph 2.3), the presence of artificially created micro-dimples can significantly affect friction and wear behaviour of mating surfaces behaving as traps of debris, reservoirs of lubricant, and pressure pockets. The introduction of specific textures may store wear particles, thus reducing the ploughing and deformation components of friction, and may also promote the retention of a lubricant film between mating surfaces, thus reducing thermal dissipations and increasing the lifetime of the sliding contacts.

Among the various manufacturing techniques, LST [7] offers promising peculiarities (fast processing time, clean to the environment, no need of vacuum, excellent control of the shape and size of the micro-dimples) so as to stimulate a line of research that deals about the possibility to replace buffer material like bronze in engine components, evaluating the impact of innovative LST technique on metal-to-metal contacts in terms of improvement of tribological properties and decreasing production costs.

An intensive pin/ball-on-disk campaign was carried out in order to test the tribological performances of 30NiCrMo12 nitriding steel suitable for the realization of engine components, like piston-rings, piston-pins and connecting rods. Samples for tribological tests were prepared as disks 26 mm in diameter and 8 mm thick. All the disks were first lapped to reach a surface roughness of 0.04 µm Ra, then were textured by regular arrays of circular micro-dimples with a diameter of 100 µm, a depth of 50 µm and a surface density of 40% (Fig. 4.1).
The experimental analysis was carried out comparing the performances of textured and untextured surfaces under the same tribological conditions, repeating each individual test in order to verify the reproducibility of the results. Three different configurations were investigated. In “full lubrication” configuration, the mating counterparts were full immersed in a bath of a commercial oil (Fig. 4.2 (a)). In “single drop” configuration, only a drop of commercial oil (concentrations lower than $2 \times 10^{-3}$ ml cm$^{-2}$) was applied between the sliding surfaces (Fig. 4.2 (b)). In “dry” contact configuration, no oil was used.
4.1.1 “Full lubrication”

Average values of friction coefficients (considering standard deviations as error bars) were summarized in the form of a Striebeck curve (Fig. 4.3), obtained showing the friction coefficient as a function of Striebeck parameter, calculated as the ratio between \( v \) (linear speed) and \( W \) (nominal contact pressure) and assuming the lubricant viscosity (\( \eta \)) as constant. Pin-on-disk mode was exploited. Conformal contact was obtained by using a smooth stainless steel pin (0.04 \( \mu \)m Ra) as static counterpart with a round contact area of 5.5 mm in diameter. Thus, the nominal flat-on-flat contact pressure was roughly 0.2 MPa. Different mating speeds (ranging from 0.06 cm s\(^{-1}\) to 40 cm s\(^{-1}\) ) were explored applying a constant normal load (4.5 N), thus ranging the Striebeck parameter roughly between 0.3 and 200 cm s\(^{-1}\) MPa\(^{-1}\).

**Figure 4.3:** Comparison of Striebeck curves in “full lubrication” configuration between textured (blue circles) and untextured (red squares) steel surfaces.

During the whole experimental analysis, both systems (textured and untextured) operate in hydrodynamic lubrication regime because of the massive presence of lubricant, even when the tribological conditions became more severe (low speeds, and Striebeck parameter lower than 10 cm s\(^{-1}\) MPa\(^{-1}\) ).
The trend of the curves reported in Fig. 4.3 (roughly constant) shows no significant transition towards boundary or mixed lubrication regimes. Nevertheless, a textured surface exhibits considerable lower friction coefficient than untextured surface. The reason is ascribable to the higher hydrodynamic lift ensured by the micro-dimples regularly distributed on the contact area, thus capable to behave as integrated pressure pockets [8].

Subsequently an endurance test was performed on both textured and untextured disks. In this case the tribometer was configured in ball-on-disk mode: static counterpart was a stainless steel ball (diameter: 4 mm), and the test was carried out applying a normal load of 4 N (the nominal contact pressure reaches about 1 GPa estimating by Hertzian model: recall paragraph 1.2, eq. (1.4)). Mating counterparts slid for 4 hours at a sliding speed of 40 cm s⁻¹. Friction coefficient evolution was monitored during the test and the results are reported in Fig. 4.4 as a function of number of laps. The textured surface maintains lower friction coefficient values for the whole endurance test with respect to the untextured surface.

![ENDURANCE TEST](image-url)

*Figure 4.4:* Endurance test in “full lubrication” configuration: comparison of the evolution of the friction coefficients (plotted as a function of the number of laps) relative to textured (blue line) and untextured (red line) steel surfaces.
4.1.2 “Single drop lubrication”

Pin-on-disk mode was exploited. Normal loads in the range 1-10 N were applied at surfaces, which slid at constant linear speeds of 1 and 12 cm s⁻¹. Conformal contact was obtained by producing a 100Cr6 steel custom pin of with a surface roughness of 0.04 µm Ra, and a round contact area of 1.2 mm in diameter. Thus, the nominal contact pressure was ranged roughly between 1 and 10 MPa.

Friction behaviours of 100Cr6 steel pin sliding against 30NiCrMo12 nitriding steels, textured and untextured, at different normal loads (from 1 N to 10 N), are shown in Fig. 4.5. Up to 2 N of normal load, friction coefficient of both textured and untextured surfaces range between 0.1 and 0.2. Increasing the normal load, untextured surface exhibits larger values of friction coefficient with high noise signal (Fig. 4.5 (a)), while textured surface presents constant and smooth friction coefficient values lower than 0.2 (Fig. 4.5 (b)).

Figure 4.5: Pin-on-disk tests in “single drop lubrication” configuration: comparison of the evolution of the friction coefficients relative to (a) untextured (red lines) and (b) textured (blue lines) steel surfaces. Tests were performed at a constant linear speed (12 cm s⁻¹), and different applied normal load: 2N (continuous lines) and 10 N (dotted lines).
Final values of friction coefficients at different normal loads and sliding velocities for textured and untextured surfaces were summarized in the form of Stribeck curve (Figure 4.6), by which it is possible to identify the different lubrication regions. Stribeck curve is obtained showing the friction coefficient as a function of Stribeck parameter, calculated as the ratio between \( v \) (the sliding velocity) and \( W \) (the nominal contact pressure), assuming the lubricant viscosity (\( \eta \)) as constant.

![Figure 4.6: Comparison of Stribeck curves in “single drop lubrication” configuration between textured (blue circles) and untextured (red squares) steel surfaces.](image)

The transition from hydrodynamic to mixed lubrication regime for untextured surface is obtained for a Stribeck parameter of about 4 cm s\(^{-1}\) MPa\(^{-1}\): for larger values, untextured surface operates in hydrodynamic regime, for lower values it operates in mixed or boundary lubrication regime.

On the contrary, Stribeck curve relative to textured surface presents a minimum value for a Stribeck parameter between 2 cm s\(^{-1}\) MPa\(^{-1}\) and 3 cm s\(^{-1}\) MPa\(^{-1}\). However, as already shown by Kovalchenko et al. [9], no transition was observed for textured surface, and the system operated in hydrodynamic regime for all applied loads due to the presence of micro-dimples at the interface between pin and disk [10].
An endurance test was also realized on untextured and textured surfaces to check the ability of textured surface to maintain low friction coefficient value for long time (8 hours). Fig. 4.7 shows the results obtained for both surfaces at a sliding velocity of 12 cm s\(^{-1}\) and normal applied load of 7 N. Textured surface shows constant and smooth friction coefficient during all the test.

![Endurance Test Graph](image)

**Figure 4.7:** Endurance test in “single drop lubrication” configuration: comparison of the evolution of the friction coefficients (plotted as a function of the number of laps) relative to textured (blue line) and untextured (red line) steel surfaces.

SEM images on textured and untextured surfaces are shown in Fig 4.8. Wear track is more evident on untextured surface with respect to the textured one (Fig. 4.8 (a) and (b)). The untextured surface exhibits wear debris and oil traces in the track (Fig. 4.8 (a')).

High instability of friction coefficient curve and seizing on untextured surface are related to the presence of debris at the contact sliding area. Wear debris gradually aggregate and transform the oil into highly viscous gel, which it is well known that in some cases terminates effective lubrication [11].
Friction coefficient increasing, observed on untextured surface for Strubeck parameters lower than 4 cm s\(^{-1}\) MPa\(^{-1}\), reflects the transition from lubricated to dry sliding [12]. On the contrary, on textured surface aggregates have not been observed at the interface between pin and disk (Fig. 4.8 (b')). Lubricant and wear particles fill the micro-dimples that work like traps, maintaining low friction coefficient between pin and textured surface during sliding [13,14].

**Figure 4.8:** SEM images of steel surfaces after the endurance test performed in “single drop lubrication” configuration.  
**a)** Wear track relative to untextured surface: red square indicates the scanned area of the enlarged detail (a’).  
**b)** Wear track relative to textured surface: blue square indicates the scanned area of the enlarged detail (b’). Arrows indicate the sliding direction of the static counterpart.
The chemical compositions of textured and untextured surfaces were examined by Energy Dispersive Spectroscopy (EDS). Principal results are shown in Tab. 4.1. Four different zones were analyzed: wear track in the untextured surface, wear track in the laser textured area outside micro-dimples, wear track inside micro-dimples, and raw surface.

On textured surface, the spectra recorded inside micro-dimples show the significant presence of Mg and Ca signals revealing the retention of the lubricant oil, while the spectra obtained on wear track outside micro-dimples are similar to those recorded on raw surface. This comparison support the idea of micro-dimples acting as lubricant reservoirs [12].

Conversely, no lubricant markers were revealed in correspondence to the wear track obtained on untextured surface, where the recorded spectra also exhibit the lacking of Nitrogen signal (expected to be found due to surface nitriding). In order to explain this behaviour, we noted a higher surface abrasion of the custom pin at the end of the test on untextured surface with respect to textured surface case.

The absence of Nitrogen signal on untextured surface could be ascribed to the presence of wear debris deriving from pin counterpart that cover the surface, shielding the signal from it.

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Table 4.1: EDS results.
4.1.3 “Dry” contact

In “dry” configuration, steel pin slid against 30NiCrMo12 nitriding steel “steady state”. Friction coefficient was large on both textured and untextured surfaces (Fig. 4.9 (a)). For a normal load of 1 N, friction coefficient is initially low (about 0.3) for each coupling (Fig. 4.9 (b)). In the case of untextured surface, it quickly rises up to 1.0 and then stabilizes, with high noise. In the case of textured surface it increases more slowly. Increasing the normal load to 3 N both textured and untextured couplings present seizure.

Figure 4.9: Pin-on-disk tests in “dry” contact configuration. a) Comparison of the evolution of the friction coefficients relative to untextured (red line) and textured (blue lines) steel surfaces. b) Expanded initial region (yellow rectangle).

Tests were performed at a constant linear speed (12 cm s\(^{-1}\)), and a constant applied normal load (1N).

SEM images on textured and untextured surfaces are shown in Fig. 4.10. The differences of the wear tracks on the two surfaces are related to the presence of wear debris at the interface between pin and disk (see “white” signal on SEM images). Looking to the untextured surface we note a spread of debris that cover the whole wear track (Fig. 4.10 (a) and (a’)). The wear track is
clearly evident also on textured, however it doesn’t show wear debris on surface among micro-dimples (Fig. 4.10 (b)). The SEM image of one micro-dimple (Fig. 4.10 (b’)) exhibits “white” signals due to irregular particles inside the hole. This indicate that wear debris move from contact region filling micro-dimples. In this case micro-dimples work like reservoirs of debris that leave free interface between pin and disk, thus reducing wear [14]. High values of friction coefficient recorded on untextured surface can be ascribed to the presence of wear debris at the contact region. Although it has been reported that wear particles at the contact zone may have the opposite effects of reducing or increasing wear [15], these latest results confirm that the presence of wear debris in the contact under study accelerates wear.

Figure 4.10: SEM images of steel surfaces after the endurance test performed in “dry” contact configuration. a) Wear track relative to untextured surface: red square indicates the scanned area of the enlarged detail (a’). b) Wear track relative to textured surface: blue square indicates the scanned area of the enlarged detail (b’). Arrows indicate the sliding direction of the static counterpart.
In summary:

- Tribological effects of laser micro-dimpling on 30NiCrMo12 nitriding steel were investigated by measuring friction coefficients with a pin-on-disk machine. Under similar operating conditions, texturing was observed to reduce friction coefficient and wear, with respect to untextured surface.

- In “full lubrication” configuration, micro-dimming ensures an improvement of friction behaviour ascribed to the well known hydrodynamic lift effect ensured by micro-dimples. Average friction coefficients were observed to be half-reduced comparing untextured and textured surfaces.

- In “single drop” configuration, micro-dimpling ensures even better performances due to oil-holding and debris-trapping capabilities determining both friction and wear reduction. In particular, under mixed lubrication regime and more severe sliding contact condition, friction coefficients are reduced of about 75% from untextured to textured surface. These good results could suggest the idea of replacing buffer bronze material for engine components working in similar operating conditions, like piston-pins and connecting rods, with metal-to-metal contacts treated by LST technique.

- In “dry” contact configuration friction coefficients are reduced of about 10% from untextured to textured surface. Debris are observed in contact region between pin and disk. In the case of textured surface they fill micro-dimples, and this process contributes to the improved tribological performances of those surfaces.
4.2 20MnCr5 textured steel coated with CrN

The strategies for the achievement of better performances and durability lately move towards a new frontier: tribologists and surface engineers have recently spent effort to evaluate the opportunity of innovative combinations of tribological coatings (hard thin films, cermets, solid lubricant, “intelligent” multicomponent) with high-precision micro-texturing [16].

LST is usually adopted in this sense, because of the capability to ablate almost all kind of materials. Recent experimental studies took into consideration TiN, TiCN, DLC, and cemented carbides coatings [17-22] demonstrating that the lifetime of them can be increased even by factors of 10 by laser patterning. Voevodin et al. [23] studied the benefit due to laser induced micro-grooving on a functionally gradient Ti-TiC-TiC/DLC coating with an upper layer of tough nanocrystalline/amorphous composite used for load support, crack prevention, and stress equalization. Micro-grooves were finally filled with MoS2 to provide a solid lubricant reservoir in the lateral dimension of the coating: this design allows to increase the wear life by at least one order of magnitude. Another application was remarkably showed by Dumitru et al. [21], who investigated laser texturing of wear-resistant DLC films by coating of already textured substrates (indirect processing) and by direct laser processing of deposited DLC films. They showed the trapping role of micro-dimples filled by abrasive wear debris, thus preventing the breakdown of the tribological system.

In an explorative and preliminary work stimulated by the previously mentioned ones, the tribological behaviours of textured steels coated by a thin CrN film were tested. Indirect laser processing was exploited: samples made of 20MnCr5 (a steel adopted for oleodynamic engine applications) were prepared as disks 50 mm in diameter and 4 mm thick. All the disks were first lapped to reach a surface roughness of 0.04 µm Ra, then were textured by regular arrays of circular micro-dimples with a diameter of 50 µm, a depth of 10 µm and a surface density of 40%.

Both textured and untextured surfaces were finally coated by a (3.5±0.3) µm thick CrN film grown by DC Magnetron Sputtering (Fig. 4.11), following the recipe that was optimized by Capotondi et al. [24,25]: principal parameters are detailed in Table 4.2.
Figure 4.11: SEM images. a) Detail of a “FIB-micro-cross-section” obtained on untextured steel surface coated with a CrN thin film. b) 52° tilted top view of laser textured steel coated with a CrN thin film. Blue rectangle indicate the “FIB-micro-cross-sectioned” area successively imaged (c): black dotted line indicate the edge of the micro-dimple.

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<tr>
<td>Substrate Temperature</td>
<td>200°C</td>
</tr>
<tr>
<td>Rotative speed</td>
<td>12 rpm</td>
</tr>
<tr>
<td>DC Magnetron setups</td>
<td>$V = 300\ V - I = 1.5\ A - W = (75\pm 5)%$</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>0.3 nm/s</td>
</tr>
</tbody>
</table>

Table 4.2: Principal deposition parameters. CrN thin films (final thickness: $(3.5\pm0.3)$ µm) were grown onto both textured and untextured 20MnCr5 steel disks.
Further tribological characterization was made subjecting both CrN coated disks (textured and untextured) to a performance test. Tribometer was configured in pin-on-disk mode: conformal contact was ensured by a custom 100Cr6 steel pin with a surface roughness of 0.04 µm Ra, and a round contact area of 2 mm in diameter. An ascending ramp was set, ranging normal load from 4 N to 12 N with increments of 2 N at intervals of 10 minutes. Mating counterparts slid in absence of lubricant for 50 minutes at a sliding speed of 50 cm s$^{-1}$.

Friction coefficient evolution was monitored during the test and the results are reported in Fig. 4.12 as a function of elapsed time. Coherently with the previous conclusions (recall paragraph 4.1), micro-texturing involves a small, but appreciable, stability and reduction of friction coefficient although to a lesser extent than that observed in lubricated contact configurations.

![Figure 4.12: Performance test carried out on CrN coated steels: comparison of the evolution of the friction coefficients relative to textured (blue line) and untextured (red line) surfaces.](image-url)
In the absence of lubricant, the hydrodynamic contribute due to texturing vanishes and the role of micro-dimples is reduced to that of trapping debris. In the present case, rather than in terms of consistent minimization of frictional dissipation, micro-texturing seem to have a considerable impact on wear mechanisms.

Fig 4.13 portrays the comparison among SEM images obtained in correspondence of wear tracks relative to untextured (Fig. 4.13 (a) and 4.13 (a')) and textured (Fig. 4.13 (b) and 4.13 (b')) samples.

Textured surface does not exhibit any site characterized by local delamination of the CrN thin film, while untextured surface reveals a more severe damage, ascribable to abrasive processes. Inside wear tracks, spalled or scuffed islands are clearly visible: CrN thin film is completely removed (Fig. 4.13 (a) and 4.13 (a')).

On the contrary, micro-texturing can inhibit, or at least delay, abrasive wear modes. Fig 4.13 (b) highlights the accumulation of wear debris inside the micro-dimples: those debris are probably due to the degradation of static steel counterpart, rather than the wear of CrN coating.

Moreover, a FIB “micro-cross-section” was obtained in correspondence of the edge of a filled micro-dimple (Fig. 4.13 (b), blue square) and then imaged by SEM (Fig. 4.13 (b')) revealing that CrN thin film is not delaminated neither inside the micro-depression, where only few traces of fatigue wear (microcracking: see Fig. 4.13 (b’) black circle) are evident and circumscribed below the elbow of the micro-dimple.
Figure 4.13: SEM images. a) 52° tilted top view: wear track relative to untextured steel surface coated with a CrN thin film. Spalled or scuffed regions are clearly visible. Red square indicates the successively scanned area (a’): the 52° tilted enlarged detail highlights the complete delamination of CrN thin film due to abrasive wear. b) 52° tilted top view: wear track relative to laser textured steel surface coated with a CrN thin film after performance test (dark arrow indicates the sliding direction of static counterpart). Blue rectangle indicates the “FIB-micro-cross-sectioned” area successively imaged (b’). White arrow indicates CrN/steel interface: no delamination is appreciable. Blue arrow indicates the accumulation of abrasive wear debris inside the micro-dimple. Black circle highlights few traces of microcracking (ascribable to fatigue wear) circumscribed at the elbow of the micro-depression.
4.3 References

Chapter 4 - Tribological behaviour of laser surface textured steel


Chapter 5

Collateral effects induced by Laser Surface Texturing

This chapter reports recent results (Tribology International, 2008: in press) regarding a study on the “collateral effects” induced by Laser Surface Texturing (LST) on nitriding steel: the aim of the work is focused on the local sub-surface impact of laser micro-ablation, during which other heat promoted phenomena take place. Morpho-structural and mechanical modifications were revealed by both FIB- and AFM-based characterizations. Moreover, a new theoretical model was proposed to interpret the grain size variation and the correlated hardening effect, as a consequence of laser-steel interaction.

5.1 30NiCrMo12 textured steel: sub-surface characterizations

Several classes of tribological experiments were developed in order to investigate the benefits of LST in terms of transition between different lubrication regimes, reduction of friction coefficients and reduction of wear rates, mainly on steel surfaces (recall paragraphs 2.3, 4.1, and 4.2).

However, the present work intends to face another specific aspect of this topic. As a matter of fact, there is a lack of information about the possible “collateral effects” of the LST process as a consequence of the interaction between laser beam and material structure. Ablation of surface is accompanied to local annealing, which could activate phase transitions in correspondence of the laser-affected zone, where the heat propagation could result in the formation of modified material layers. In fact, laser heating is well known to cause several phenomena, in particular on steel surfaces: variations in dislocations and residual stresses distributions, formation of different carbide types, size and shape modification of austenitic grains and hardening effects [1-3].

Laser textured 30NiCrMo12 nitriding steel has been studied in order to investigate laser-steel interaction in terms of morphological and structural sub-surface modifications. Focused Ion Beam (FIB) coupled with Secondary Electron Microscopy (SEM) was utilized to explore local properties by micro-sectioning and further imaging. Thanks to the versatility and ability to remove
and observe trenches of surface without introducing relevant additional damage, FIB approach is adopted to characterize sub-surface micro-cracking, defects distributions and grain structure of material surfaces (see paragraph 3.1). Sub-surface hardness measurements were also performed by indenting a “macro cross-section” of the specimen material by using Atomic Force Microscope (AFM) working in nanoindentation mode. Thanks to its ability of simultaneous high resolution indenting and imaging, this powerful tool allows to investigate the hardness distribution in sub-micrometric areas [4,5].

30NiCrMo12 nitriding steel samples were first lapped to reduce the surface roughness (Ra) to 0.04 µm, then textured by LST. Table 5.1 contains a description of the principal parameters of the laser apparatus adopted for the treatment. Textured nitride steel specimens show regular arrays of circular micro-dimples with a diameter of 100 µm, a depth of 50 µm and a surface density of 40% (Fig. 5.1).

<table>
<thead>
<tr>
<th>Laser type</th>
<th>“Spectron” Nd:YAG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser beam wavelength</td>
<td>1.06 µm</td>
</tr>
<tr>
<td>Pulses duration</td>
<td>30 ns</td>
</tr>
<tr>
<td>Laser beam energy per pulsation</td>
<td>4 mJ</td>
</tr>
</tbody>
</table>

Table 5.1: Details of the laser apparatus utilized to produce LST micro-dimpling. Laser scanning was carried out by CNC X-Y table under special program providing definite micro-texture arrays.

Figure 5.1: SEM images of 30NiCrMo12 nitriding steel textured surface. a) 45° tilted top view. b) Perpendicular “macro-cross-section” of an individual micro-dimple: the shape could be approximated as hemi-spherical.
Morphological characterization was performed using the FEI Strata\textsuperscript{TM} DB235 Dual Beam System (recall paragraph 3.1). Perpendicular “micro-cross sections” of steel surfaces (textured and untextured) were obtained using FIB ($E_{\text{beam}} = 30$ KeV) as micro-machining miller, setting 5 nA as ion beam current for first rough trench, and 1 nA for final polishing. Sub-surface discovered wall is one side of the perpendicular trench, milled by progressive steps (Fig. 5.2). In order to prevent the topmost material from mechanical intermixing upon contact with energetic ions [6], the surface sample was protected by a thin platinum layer (1 µm thickness). Pt-shield had been grown starting from a gas precursor, and using a 10 pA ion beam current that assisted local deposition. Furthermore, by tilting the sample holder, images of discovered walls were obtained collecting secondary electrons generated by FIB as primary beam at low current (50 pA), in order to take advantage of ion-channelling contrast, which is very useful for grain size analysis [7].

![Figure 5.2: Simplified sketch which summarizes the experimental procedures followed in order to carry out a morphological sub-surface characterization. SEM image (a) shows the thin Pt-shield grown in-situ, beside a micro-dimple edge, by a FIB-assisted deposition. Dotted lines represent the projection of the trench, successfully milled by FIB setting high ion current mode. Thus, a “micro-cross section” was gained by progressive rastering steps: white arrow indicates the relative depth profile (b). Sub-surface discovered wall was imaged using FIB as primary probe (low current mode), by tilting the sample holder.](image)

 Afterwards textured samples were perpendicularly cut with a saw, in order to obtain “macro-cross sections” and then polished with SiC papers and diamond slurry (up to 0.05 µm Ra). Micro-indentation grids were finally performed on these samples on selected areas around micro-dimples (Fig. 5.3), by using a Digital Instruments EnviroScope Atomic Force Microscope (provided by Veeco\textregistered) working in nanoindentation mode, in order to indent the sample and image it right after the indentation.
Figure 5.3: Simplified sketch which summarizes the experimental procedures followed in order to carry out a mechanical sub-surface characterization of “macro-cross sectioned” textured steel samples. A micro-indentation grid was realized, and successfully imaged by AFM on selected areas around dimple edges. Spacing between two adjacent indentations ($a \approx 1 \mu m$) is maintained constant, but could slightly change in proximity of the border, in order to faithfully follow the shape of the dimple edge.

All the indentations were performed by a Berkovich diamond tip mounted on a sapphire cantilever (the whole probe had been assembled and provided by Micro Star Technologies®) under the same conditions; in particular the load applied on the sample was 1.5 V in terms of photodetector voltage. Thus, considering the cantilever stiffness (5085 N/m) and the deflection sensitivity (130 V/nm), a maximum indentation load of about 992 $\mu N$ was estimated. Further details on this setup are reported in [5]. Finally, the indented area was imaged using a standard AFM tapping probe (MPP-11100-Tap300 Metrology Probes by Veeco®) in order to measure the projected contact area in a direct way and thus evaluate the hardness just dividing the maximum applied load by this area. This approach allows to solve the pile-up problem, which affects the results obtained by the Oliver-Pharr method [8-10]. The Oliver-Pharr method guarantees hardness measurement without imaging the indentation impression, since it establishes a relationship between the projected area of the indentation impression, the maximum depth of indentation ($h_{max}$), and the initial unloading stiffness (S), where $h_{max}$ and S are both measurable from the load-displacement curve. However, the Oliver-Pharr method quite overestimates the hardness values when the pile-up effect is not negligible, such in this case. With AFM Nanoindentation, since it is possible to measure directly the contact area, the actual presence of pile-up can be take into account [5].
5.1.1 Sub-surface morphological characterization

Fig. 5.4 (a) shows a FIB image obtained in correspondence of a FIB milled “micro-cross-section” on untextured steel. Discovered wall extends 20 µm in width and 7 µm in depth. Ion-channelling contrast allows appreciation of a homogeneous sub-surface structure: clear defined boundaries delimit large domains (areas: up to 10 µm²) which include isolated features (“dark” signals) of round or polygonal shape (sizes: 200-300 nm). These features could be associated to steel porosity or C/N-compounds. The possible presence of carbides and nitrides is justified by the not negligible presence of Cr an C dispersed in steel, or ascribable to nitriding process.

![FIB images](image1.png)

Figure 5.4: FIB images obtained by tilting samples after sub-surface FIB micro-trenches milled on 30NiCrMo12 nitriding steels. a) Untextured surface. b) Textured surface: micro-dimple edge is visible on the top-right corner.

FIB milled “micro-cross sections” were also obtained beside micro-dimples on textured steel (Fig. 5.4 (b)). Also in this case, discovered walls are 7 µm deep and 20 µm wide from micro-dimples edge. Sub-surface morphology of textured steel exhibits a radically different scenario with respect to the untextured one. Moving from micro-dimple edge to bulk steel for about 5 µm in radial coordinates, it appears a dense distribution of small grains with irregular boundaries, whose areas range from 0.01 µm² to 0.5 µm²; while moving further toward bulk steel, it appears a grain pattern similar to the previously observed for the untextured case (Fig. 5.4 (a)): larger domains (areas: 5-10 µm²) with polygonal boundaries and “dark” inclusions are recognizable. Therefore, a grain size reduction is observed in correspondence of laser affected zone, suggesting the occurrence of phase transition phenomena induced by laser heating. This observation is in agreement with the results reported by Obergfell et al. [1]. The modified material layer was observed in a few microns spacing; this further observation leads to quantify the radial width of the Heat Affected Zone (HAZ)
in agreement with the 2D calculations recently published by Valette et al. [11]. The radial spread of thermal effects strongly depends on the laser pulse duration, and it is confined in the range of 5-10 µm whenever the interaction time lasts few tens of nanoseconds (such in the present case).

5.1.2 A new model for grain size distribution

A new theoretical model was developed to interpret the grain size behaviour observed in laser-affected zones. The energy $W$ of the laser is dissipated in a fraction $\varphi_h$ for producing an individual micro-dimple, in a fraction $\varphi_m$ for modifying the material structure around the micro-dimple, and in a fraction $1 - \varphi_h - \varphi_m$ in other processes. Indicating with $\Phi$ the energy spent per unit volume for creating the micro-dimple (a “material constant”), and with $W_h$ the actual energy spent for creating an individual micro-dimple, we have: $W_h = \varphi_h W = \Phi V_h$, where $V_h = \pi R^2 H f$ is the volume of the micro-dimple having radius $R$ and height $H$ (Fig. 5.5).

$$f(R, H) = \left(\frac{H}{R} - \frac{H^2}{3R^2}\right)$$

Figure 5.5: Simplified sketches which summarize the two geometries, involved in the theoretical model. a) Cylindrical; b) Spherical. Both approaches imply radial coordinates ($x$) originating from the surface of the micro-dimple, whose height ($H$) is defined as maximum depth.

$f$ is a shape function that equals 1 for the cylindrical shape (Fig. 5.5 (a)), whereas $f(R, H) = \left(\frac{H}{R} - \frac{H^2}{3R^2}\right)$ for different spherical shapes (Fig. 5.5 (b)). Note that $R$ for a spherical micro-dimple is here defined as the radius of the osculating sphere, and not as the radius of the base of the related spherical cap. Accordingly, the lateral surface of the micro-dimple is $S_h = 2\pi RH$, independently from its shape.
\( \gamma \) indicates the total surface energy per unit area required to produce new grain boundaries, having: \( W_m = \varphi_n W = \gamma S \), where \( W_m \) is the total energy required to produce new grain boundaries, and \( S \) is the total surface of the grains. Locally, the energy balance becomes: \( -\frac{dW_m(x)}{dx} = \gamma \frac{dS(x)}{dx} \), where \( x \) is the radial coordinate which has the origin at the surface of the micro-dimple.

The energy penetration into the material is dictated by its absorption coefficient \( k \), according to \( W_m(x) = W_n e^{-kx} \), where \( x \) is the penetration coordinate. Moreover the number of grains in the region comprised between \( x \) and \( x+dx \) is \( dN = \frac{2\pi(R+x)(H+\delta\chi)dx}{d^3} \), where \( \delta = 0 \) for cylindrical micro-dimples or \( \delta = 1 \) for spherical micro-dimples and \( d \) is the grain size. The surface of each grain is \( s = \alpha d^2 \), where \( \alpha \) is a shape constant (e.g. for cubic grains \( \alpha = 6 \)). Thus, the total surface is \( dS = sdN = \frac{2\pi(R+x)(H+\delta\chi)\alpha dx}{d} \). Accordingly, from the previous local energy balance, the grain size variation is derived in the following form:

\[
d(x,R,H) = \frac{2\pi\alpha(R+x)(H+\delta\chi)}{W_n ke^{-kx}} = \frac{2\gamma\alpha\varphi_h}{\Phi \varphi_n kR f(R,H)} \left(1+x/R\right)
\]

(5.1)

Note that, mathematically, \( d(\infty,R,H) = \infty \) since no energy is available for grain boundary formation at infinity and:

\[
d(0,R,H) = \frac{2\gamma\alpha\varphi_h}{\Phi \varphi_n kR f(R,H)} \frac{1}{\sqrt{\pi\Phi H f(R,H)}}
\]

(5.2)

that is thus predicted to scale inversely to the size of the micro-dimple. Similarly \( d(x,0,H) = \infty \) since a vanishing size of the micro-dimple implies a vanishing laser energy, whereas \( d(x,\infty,H) = 0 \), that is, infinitely small grains can be developed using infinite energy. Indeed, note that the size of the micro-dimple is related to the laser energy by:

\[
R = \sqrt{\frac{\varphi_h W}{\pi\Phi H f(R,H)}}
\]

(5.3)

e.g., for self-similar micro-dimples (\( R \propto H \)) \( R \propto W^{1/3} \).

Further considerations are necessary in order to identify the limits of validity for this theoretical approach. The model is based on the energy balance that governs the laser-matter interaction, but it does not invoke a time-dependence relationship, neither it explains the direct role
of temperature. Thus, the proposed approach cannot predict the nature of the sub-surface phase transitions occurring as “collateral effects” due to LST. It is difficult to clarify this point, anyway it can be useful to recall some well known conclusions from metallurgical studies [12-14].

Metal melting, matter re-deposition, and re-crystallization processes occur in the nanosecond-pulse duration regime, as already mentioned in literature [12,13]. Conversely, in the femtosecond case the ultra-short duration of the pulses leads to largely reduced laser-matter interactions, and forces other types of phase transition phenomena, such as sublimation. In this regime, which is well suited for micromachining at the sub-micron scale [14], thermal damage is minimal and the HAZ becomes not trivial to recognize with FIB/SEM approach. It is thus necessary to adopt a STEM (Scanning Transmission Electron Microscopy) to highlight lattice damage due to mechanical stresses [3]. Therefore, it can be argued that the phenomenology related to the fs-regime is beyond the limits of the proposed model.

In the present case (Fig. 5.1 (b)), the shape of the micro-dimple could be approximated as hemi-spherical \((R = H = 50 \, \mu m)\), because the radius of the osculating sphere coincides with the radius of the micro-dimple. Thus, eq. (5.1) can be used to fit experimental data in a simplified form, making opportune substitutions \((f = 2/3; \delta = 1)\):

\[
d(x) = d_0 \left(1 + \frac{x}{R}\right)^2 e^{kx} \tag{5.4}
\]

where coefficients \(k\) and \(d_0 = \frac{3\gamma \alpha \rho_s}{\Phi \rho_m kR}\) will be gained as best fit parameters.

Grain analysis was carried out on several FIB images of different discovered walls trenched beside micro-dimples (see an example in Fig. 5.4 (b)), in order to obtained a statistic collection: up to 80 grains were characterized. Note that model is based on the assumption of constant laser energy \(W\), and does not take into account other phenomena such as FIB-induced re-annealing during Pt-shield deposition.
Grain analysis results are shown in Fig. 5.6, where best fit function is plotted with experimental data. Average sizes ($d$), calculated as square root of grain areas, were plotted against radial distances ($x$) of the center of each grain from micro-dimple edge. The distribution is fitted by eq. (5.4), obtaining $d_0 = (0.24 \pm 0.03) \, \mu m$ and $k = (0.23 \pm 0.02) \, \mu m^{-1}$ as best fit parameters.

![Grain size behaviour](image)

**Figure 5.6**: Diamonds: lateral grain sizes ($d$) plotted against radial distances ($x$). Dotted line: best fit of the experimental data by eq. (5.4); $d_0 = (0.24\pm0.03) \, \mu m$ and $k = (0.23\pm0.02) \, \mu m^{-1}$ are the best fit parameters.
5.1.3 **Sub-surface mechanical characterization**

The experimental analysis on “macro-cross sectioned” textured steel consists on several matrices of indentations performed on a 20x20 μm² selected area around an individual micro-dimple edge. The distance between two contiguous indentations is about 1 μm (this distance could slightly change in proximity of the border, in order to faithfully follow the shape of the micro-dimple edge). The hardness map is reported in Fig. 5.7.

![Hardness map](image)

**Figure 5.7:** Hardness map relative to a sub-surface 20x20 μm² area of the “macro-cross-sectioned” textured steel: hardness values (see color scale) are represented according to the distance from the top surface and the position along the lateral direction. AFM-nanoindentation campaign (recall Fig. 5.3) consists on several matrices performed around an individual micro-dimple edge (top-right).

Hardness profile replies the sub-surface morpho-structural trend of laser affected-zones previously described: hardening occurs as a further consequence of laser-matter interaction, locally confined in HAZ. Another representation of the AFM-nanoindentation data is reported in Fig. 5.8: average values of hardness (H) are plotted against radial distances (x) from micro-dimple edge (error bars are standard deviations). Moving towards micro-dimple edge hardness values increase by a factor of 2, moving from 3500-4000 MPa (for a distance of about 20 μm from micro-dimple edge) up to 7000-7500 MPa (for a distance of about 2 μm from micro-dimple edge).
Figure 5.8: Circles: local hardness (H) plotted against radial distances (x). Dotted line: best fit of the experimental data by eq. (5.7); \( h^* = (1690\pm110) \text{ MPa} \mu\text{m}^{0.5} \) and \( H^* = (3450\pm80) \text{ MPa} \) are best fit parameters. Continuous line: best fit of the experimental data by eq. (5.8); \( h^{**} = (1450\pm200) \text{ MPa} \mu\text{m}^{0.6} \), \( H^{**} = (3600\pm150) \text{ MPa} \) (coherent with \( H^* \) value), and \( \beta = 0.6\pm0.1 \) (coherent with 0.5 exponent) are the best fit parameters.

The final discussion covers the relationship between grain size reduction and hardness increment accordingly to the Hall-Petch behaviour [15,16]:

\[
H(x, R, H) = H_\infty + h d(x, R, H)^{-\beta} e^{-k x}
\]

where \( h \) is a constant and \( H_\infty = H(x = \infty) \) represents the hardness of the untextured material. Note that in terms of energy and for self-similar micro-dimples, an hardness scaling near the micro-dimples has to be taken into consideration: \( H(x = 0, W) = H_\infty + \bar{h} W^{-1/6} \) (with \( \bar{h} \) constant).
Introducing eqs. (5.1) and (5.2) into eq. (5.5), yields:

\[ H(x, R, H) = H_x + h d(0, R, H)^{-1/2} \frac{e^{-kx/2}}{\sqrt{1 + x/R(1 + \delta x/H)}} \]  

Eq. (5.6) could be reduced in two simpler forms, which are useful to fit the experimental data. Reminding the hemi-spherical approximation \((R = H = 50 \, \mu m; f = 2/3; \delta = 1)\), and introducing eq. (5.4), \(k\), and \(d_0\) best fit parameters previously gained into eq. (5.5), yields:

\[ H(x) = H_x + h d_0^{-1/2} \left( 1 + \frac{x}{R} \right)^{-1} e^{-kx/2} \]  

(5.7)

or, introducing an exponential terms \((\beta)\) that will be gained as additional best fit parameter and is expected to be close to 0.5:

\[ H(x) = H_x + h d_0^{-\beta} \left( 1 + \frac{x}{R} \right)^{-2\beta} e^{-kx} \]  

(5.8)

where parameters \(H_x\) and \(h\) will be gained as best fit parameters. Therefore, the experimental data were fitted by using each of the two last custom equations. Note that eq. (5.7) faithfully obeys to the Hall-Petch’s law, while eq. (5.8) includes the term \(\beta\) which identifies the agreement between the system behaviour and the Hall-Petch’s law.

Results are shown in Fig. 5.8, where the numerical fits are plotted with experimental data. Fitting the data by eq. (5.7), \(h^* = (1690 \pm 110) \, MPa \, \mu m^{0.5}\) and \(H_x^* = (3450 \pm 80) \, MPa\) were obtained as best fit parameters (dotted line); while fitting the same by eq. (5.8) \(h^{**} = (1450 \pm 200) \, MPa \, \mu m^{0.6}\), \(H_x^{**} = (3600 \pm 150) \, MPa\) (coherent with \(H_x^*\) value), and \(\beta = 0.6 \pm 0.1\) (coherent with the 0.5 exponent of the Hall-Petch’s law) were obtained as best fit parameters (continuous line).

Thus, the two best fit functions are very similar and in good agreement with hardness experimental distribution, thus experimental data are consistent with the Hall-Petch’s law.
In summary:

• An experimental work was carried out on 30NiCrMo12 nitride steel micro-dimpled by a Nd:YAG ns-pulse duration laser beam in order to discover and explain sub-surface “collateral effects” due to LST. Laser ablation in creating micro-dimples is accompanied to local heating which promotes the formation of a modified material layer confined in HAZ: morphological, structural and mechanical changes occur in micrometric sub-surface areas near the micro-dimple edge.

• Grain analysis was performed on FIB images: channelling contrast revealed domains distribution, whose dimensions strongly decreased on textured steel moving from bulk to micro-dimple edges. A theoretical model was proposed to interpret grain size behaviour according to the properties of textured material, to the characteristics of laser beam and to the geometry of ablated micro-dimples.

• AFM-nanoindentation campaign on “macro-cross sections” revealed an increment of hardness values, which grew up even by a factor 2 with respect to hardness values measured on bulk, accordingly to Hall-Petch behaviour: hardening was found to be correlated with grain size variation due to laser-matter interaction.

• Experimental data are in good agreement with the proposed theoretical model, that can thus be used for controlling local hardening due to LST processes carried out in ns-pulse duration regime.
5.2 References


Conclusions and outlooks

This thesis was aimed to give a scientific contribute to Tribology community, following the “state-of-the-art” lines of research finalized to the development of strategies and methods for the optimization of tribological behaviour of mating surfaces. Two parallel Surface Engineering solutions were investigated and tested on steels: innovative “tribo-coatings” and laser micro-texturing.

From the experimental point of view, Dual Beam Machine has proved to be a powerful instrument for tribological studies. The strategy of coupling Focused Ion Beam (FIB) + Secondary Electron Microscope (SEM) was utilized for sub-surface characterizations of plasma- and thermally-sprayed hard coatings, exploiting simultaneous imaging and micro-machining approaches. Experimental campaigns carried out on different classes of “tribo-coatings” allowed to correlate tribological and mechanical properties to sub-surface behaviours.

A Vickers-indentated TiO$_2$ thick layer plasma-sprayed onto C40 steel was micro-sectioned by FIB in order to verify the sub-surface microstructural alterations induced by indentation stresses (paragraph 3.2). The study revealed a remarkably irregular cracking distribution, and it also indicates significant anisotropy in material strength, casting doubts on the quantitative reliability of indentation fracture toughness measurement. This preliminary work highlights the need for further accurate investigations of sub-surface cracking behaviour during sharp indentation.

Another FIB-based study was carried out in order to compare the tribological performances of promising “Duplex” systems, where three-layered DLC-based films were are deposited onto different hard thick interlayers (namely: Ni-Cr, Al$_2$O$_3$-TiO$_2$ and WC-Co) thermally-sprayed onto C40 steel substrates (paragraph 3.3). “FIB-micro-cross-sections” obtained in correspondence of wear tracks after ball-on-disk tests reveled that friction and wear behaviours of the three-layered DLC-based film mainly depend on the properties of the interlayer, which are closely related to the temperature. At room temperature, with respect to the other interlayers the hard and tough WC-Co interlayer was observed to offer the best performance: no cracking, neither spallation phenomena were observed. On the contrary, at higher temperature, WC-Co interlayer suffered a microstructural alteration, partly losing its load-carrying ability. Conversely, the reversed behaviour relative to
Al₂O₃-TiO₂ was less straightforward to be exhaustively explained: further investigations are required.

Laser Surface Texturing (LST) technique, consisting in the modification of surface topography via regular distribution of laser-ablated micro-textures, was exploited to improve the tribological performances of mating surfaces. 20MnCr5 and 30NiCrMo12 nitriding steels were micro-dimpled by a Nd:YAG ns-pulse duration laser beam. An intensive pin/ball-on-disk campaign was carried out comparing the performance of textured and untextured samples under different lubrication configurations: the three major integrated effects due to micro-dimpling were showed and explained (paragraph 4.1). In “full lubrication” configuration, micro-texturing was observed to halve average friction coefficients: this benefit is ascribable to the well known hydrodynamic lift effect ensured by micro-dimples. In “single drop” configuration, micro-dimpling ensured even better performances due to oil-holding and debris-trapping capabilities inhibiting the transition between mixed and boundary lubrication regime, thus determining a wear damping and a remarkable friction reduction (up to 75%). These good results could suggest the idea of replacing buffer bronze material for engine components working in similar operating conditions, like piston-pins and connecting rods, with metal-to-metal contacts treated by LST technique. In “dry” contact, the minimization of frictional dissipation due to micro-texturing was observed to be less evident (around 10%). In the absence of lubricant, the hydrodynamic contribute vanishes, and the role of micro-dimples is reduced to that of trapping debris.

The same consideration could be extended to the further explorative study carried out on laser-textured steel coated with a PVD-grown CrN thin film (paragraph 4.2). In this case, micro-texturing seem to have a considerable impact on wear mechanisms, inhibiting or at least delaying abrasive scuffing phenomena. These preliminary promising results suggest to spend further efforts to evaluate the opportunity of innovative combinations of “tribo-coatings” with high-precision micro-texturing. Within this contest, future perspective of works are oriented to reproduce the same experimental protocol on different systems, taking into consideration other kinds of coatings (for example: similar nitrides such as TiAlN, or “solid lubricants” such as DLC and MoS₂) and/or varying micro-texture parameters (i.e. surface coverage, shape and size of the micro-dimples). Despite of their complexity, ad hoc wear models are also required.
Another specific aspect of LST process was investigated in order to fill the lack of information about the possible “collateral effects” of the LST process as a consequence of the interaction between laser beam and material structure (paragraph 5.1). Sub-surface FIB-based and AFM-based analysis revealed that laser ablation in creating micro-dimples is accompanied to the formation of a modified material layer confined in a heat affected zone near the micro-dimple edge, where grain size variation and hardening occurred. A theoretical model was proposed to interpret grain size behaviour according to the properties of textured material, to the characteristics of laser beam and to the geometry of ablated micro-dimples. Indeed, accordingly to Hall-Petch behaviour, hardening was found to be correlated with grain size variation due to laser-matter interaction.

These latest results pave the way towards some final considerations and outlooks. Although sub-surface fracture toughness measurement could not be performed by AFM-nanoindentation due to the unavailability of sufficiently high normal loads, laser induced hardening is expected to be correlated to a local increasing of the brittleness. Considering this hypothesis (that should be validated by further experiments, for example through microindenter-based campaigns), LST technique could be meant unsuitable for some specific applications, where both low friction and low material fragility are required. These conclusions stimulate to develop and test an alternative and competitive micro-texturing processing method. The setup of the recipe regarding UV-beam lithography coupled with electrochemical etching is work in progress.
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- Study of tribological and mechanical properties of engineered surfaces;
- Study of ion-matter interaction processes;
- Modelling of laser-matter interaction processes.
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- 34\textsuperscript{th} Leeds-Lyon Symposium On Tribology, Lyon (France), 4-7 Sept. 2007 (Oral);
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