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The effect of N on the structure, mechanical properties and tribological behaviour of TMD coatings in contact with rubber

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The effect of N on structure, mechanical properties and tribological behaviour of TMD coatings in contact with rubber

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Abstract

Transition metal dichalcogenides (TMD) coatings are solid low-friction self-lubricant materials enabling easy sliding by formation of a tribofilm at the interface in the contact region. W-S coating, which belongs to the TMDs family, was doped with N in order to combine low friction of the coating with good hardness due to addition of a third element. In this work, W-S and W-S-N coatings with different composition have been deposited by magnetron sputtering, characterised and evaluated with respect to the structure, mechanical properties and tribological performance. The composition was varied by changing the flow of N$_2$ into the deposition chamber, leading to nitrogen contents ranging from 0 to 33 at.%. All coatings were deposited with Cr interlayer. Films W-S and W-S-N deposited with the lowest content of N had a crystalline structure, while coatings with the higher N content were amorphous. The coating were tribologically tested against nitrile-butadiene rubbe (NBR) balls at room temperature and 200°C using a pin-on-disc tribometer. Energy dispersive spectroscopy, optical microscopy observations and 2D profilometry were performed after the tribological tests. The results showed that the coatings had better tribological performance at elevated temperature. The wear and friction behaviour of the coatings was interpreted as a function of several factors including: mechanical strength, structure and formation of the tribofilm. It was concluded that W-S-N coatings supposedly could be material for applications requiring contact with rubber at temperatures greater than room temperature.

Keywords: TMD; Friction coefficient; Self-lubricant; Magnetron sputtering; Coating
Resumo

Os revestimentos de Dicalcogenetos de Metais de Transição (DMT) são materiais sólidos, auto-lubrificantes com baixo-attrito que permitem um fácil deslizamento através da formação de uma camada transferência na interface da zona de contacto. Os revestimentos W-S, que pertencem à família dos DMTs, foram dopados com N de forma a combinar o baixo atrito dos revestimentos com elevada dureza, através da adição de um terceiro elemento. Neste trabalho, os revestimentos W-S e W-S-N com diferentes composições foram depositados, caracterizados e avaliados no que diz respeito à sua estrutura, propriedades mecânicas e comportamento tribológico. A composição foi variada através da mudança de fluxo de N$_2$ no interior câmara de deposição, levando a uma variação atómica em azoto nos revestimentos de 0 a 33 %. Todos os revestimentos foram depositados com uma intercamada de Cr. Os filmes W-S-N depositados com o menor teor e sem N apresentam alguma cristalinidade, enquanto os revestimentos com maior percentagem de N são amorfos. Os revestimentos foram tribologicamente testados por pino-disco com um contracorpo esférico de borracha NBR à temperatura ambiente e a 200°C. Após os ensaios tribológicos, as amostras foram caracterizadas por EDS, microscopia ótica e perfilometria 2D. Os resultados demonstraram que os revestimentos apresentam melhor performance a elevadas temperaturas. A taxa de desgaste e o coeficiente de atrito foram interpretados como função de vários fatores, incluindo: dureza, estrutura e formação da camada transferência. Deste trabalho, podemos concluir que os revestimentos W-S-N podem ser usados em aplicações que requeiram o contacto com borracha a temperaturas acima da temperatura ambiente havendo uma redução do atrito em relação ao deslizamento de metal borracha para as mesmas condições.

Palavras-chave: TMD; Coeficiente de atrito; Auto-lubrificantes; Pulverização catódica magnetrão; Revestimento
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Chapter 1
Introduction

One of the main challenge for modern technology is to limit energy losses. It is estimated that around 25% of the fuel energy in passenger cars is wasted on overcoming friction. The science and technology of interacting surfaces in relative motion, which concern topics, such as friction, wear and lubrication is so-called tribology. These topics are related to energy and wear losses as reduction of friction in mechanical systems could significantly lower energy demands [1].

Lubrication is an effective way to control friction and reduce wear. Lubricants form a protective tribofilm between interacting surfaces preventing solid/solid contact, and consequently reduce friction and wear. Lubricants are also used in order to suppress or limit the contact pressure and heat generated by friction. However, in many cases, the presence of fluid is neither possible nor recommended. Therefore, coatings which provide self-lubrication were designed and developed, becoming an effective alternative to fluid lubricants [1] [2]. For majority of tribological applications, the protection of the bulk material by thin films is a suitable method for reducing wear and friction [3]. Solid lubricants can be used in environments where fluid lubrication would be considered as a contaminant, such as in optical systems or in the food industry. Another purpose of using solid lubricants is to achieve desired mechanical, chemical, optical or electronic properties opposed to bulk properties, what enables the use of e.g. lightweight, cheaper or less wear resistant bulk materials [4] [5].

Self-lubricant coatings such as transition metal dichalcogenides (TMDs) have been in focus for several decades due to their potential use in various branches of science and technology, i.e. in aerospace technology. Mechanisms of devices for aerospace applications are designed to be used in severe condition, and at wide range of temperature.
For such applications, it is crucial to limit usage of liquid lubricants to minimum. Pure TMDs are soft and oxide easily in humid environment. In this work, in order to avoid these drawbacks as well as to provide better load bearing capacity and improve adhesion, TMDs are usually deposit in vacuum and doped with other elements. The development of doped TMD coatings provided an alternative for hard films which do not always exhibit good tribological properties [2].

Self-lubricating coatings (such as WS$_2$ or MoS$_2$) offer an in situ lubricating film without the need for an external supply of lubricant. The focus of this work will be on low-friction triboactive coatings, which activate, change and adapt their properties when exposed to a tribological contact, leading to the formation of so-called tribofilm. Such film layer is usually only a few tens of nanometers thick but has a significant positive effect on coating performance [1].

In this thesis the tribological contact between the coating and rubber was investigated, friction and wear reduction becomes highly important in the polymer processing industry since polymer articles are often produced by moulding. Problems of mould release, as well as of the build-up of deposits on the mould surface so-called mould fouling are endemic in the polymer industry. These problems significantly limit the production rate and increase cost to the industry. In order to enable easy removal of the moulded part from the mould, the mould release agent can be introduced at the contact area. Chemical agents can provide surface slip or lubricity to the mould surface, however this solution is not permanent. An effective way of correcting the situation is to use the low-friction adaptive coatings on the surface of moulds which facilitate the mould release process [6]. Such approach has been used in this work.
Chapter 2

Industrial problem

During the twentieth century polymer-based materials (rubber, plastics and composites) were as important engineering materials as traditional ceramics, timber and concrete. Polymer products are often manufactured by moulding where the material is introduced into a cavity, heated up and pressurised. Consequently, the material solidifies and the ready part is removed from the mould. Mould release is a well-known problem in the polymer processing industry. Another issue is the build-up of deposits on the mould surface known as mould fouling. Short moulding cycles compound the problem and can even hinder the automated moulded part removal process. Mould release and mould fouling problems are often associated with each other, and can be the reasons of limited production rate, necessity of mould cleaning, and significantly higher cost of production [6] [7] [8].

In the moulding process, polymer (usually in semi-liquid or liquid form) is introduced into the mould and solidified. Mould sticking depends mainly on the nature of the surface layers formed during the moulding process. Once polymer and the mould come into proximity of each other, the intermolecular attraction between them will occur resulting in their adhesion. Many polymers are chemically reactive and can form chemical interaction with the mould material. In case when such interaction does not occur, there always will be at least Van der Waals forces present between surfaces of materials in contact. For that reason, some mould sticking is inevitable. One of factor influencing the moulding material and the mould interaction is geometry of the moulding form since parts of more intricate shape will be much more difficult to release than the ones with simple shape [7].
Some examples of products which face mould sticking problem where the contact between rubber/metal or soft polymer/metal are crucial include: tire treads and hoses of intricate shape which hinders the release of the tire from the mould, or rubber seals (O-rings and others) which are easily damaged due to the high adhesion developed between the seal and the mould (Figure 2.1) [9] [10] [11].

In order to provide surface slip and lubricity to the mould surface and consequently, to allow easier removal of the moulded part from the mould, the mould release agent can be introduced to the system. However, this solution is not permanent and in some cases the mould release agent must be applied quite frequently to the system. Another solution to facilitate the mould release process and to reduce adhesion between the mould and the moulding material. Adhesion can be reduced if the surface energy of the metallic mould is reduced. This can be achieved by coating the mould with a low surface energy material [8]. Applications which require specific materials properties either in terms of thermo-mechanical or tribological behaviours have not been yet profoundly investigated. In this work, low friction coatings based on transition metal dichalcogenides (TMD) in contact with rubber have been studied.

Figure 2.1: Examples of products which face mould sticking problem due to the contact between rubber and metal: (a) rubber seals, (b) rubber hose, (c) tire treads [9] [10] [11].
Chapter 3

Tribological behaviour of rubber

The tribology of elastomers plays an important role in friction reduction necessary to minimize energy loss, decrease wear, increase lubrication, and obtain more efficient and longer lasting materials [12]. The frictional behaviour of rubber sliding against a hard substrate has a significant practical importance, e.g. for the construction of tires. Rubber possesses some unique frictional properties which metals and other polymers do not have, what is accounted for the very low elasticity of rubber, as well as its high internal friction in a broad frequency region [13].

K.L. Grosch [14] in his pioneer work has shown that friction of rubber is often directly related to the internal friction of the rubber. Therefore, experiments conducted in such way that rubber slides on silicon carbide paper and glass result in the coefficient of friction with the same temperature dependence as that of the complex elastic modulus $E(\omega)$ of rubber. This proves that the friction force is primarily a bulk property of rubber [13].

The friction force between a rough hard material and rubber has two contributions: adhesion and hysteric components. During sliding, the hysteric component results from the oscillating forces exerted by the asperities of the rough surface onto the surface of rubber. This leads to cyclic deformations of rubber and energy dissipation due to internal frictional damping. Consequently, the hysteric contribution to the friction force will have the same temperature dependence as that of the elastic modulus $E(\omega)$. The adhesion component is considered only for very clean and relatively smoother surfaces [13]. Periodical deformation of surface asperities of rubber as well as the small length scales contact with the rough hard substrate indicate the occurrence of adhesion bonds.
Since the adhesion and hysteric components are related to dynamic mechanical properties of elastomers, rubber sliding on rough hard surfaces exhibits typical viscoelastic features [15].

The adhesion force \( F_{adh} \) can be express as the relation of the viscous dissipation \((\tan\delta)\), elastic modulus \((E')\), constant dependent on the particular sliding combination \((K_2)\) and the normal pressure \((p)\). As it can be seen from the equation 3.1, although a stick-slip process occurs, adhesion also relates from viscoelastic properties of the rubber [13].

\[
F_{adh} = K_2 \left( \frac{E'}{p} \right) \tan\delta
\]  

(3.1)

Low elastic modulus of rubber often causes surface instabilities during sliding at high velocities and for very smooth surfaces. The most well-known instabilities so-called Schallamach waves involve a compressed rubber surface in the front of the contact area with hard rough material undergoing buckling what forms detachment waves on the surface of soft rubber [16].
Chapter 4

Transition metal dichalcogenides

Transition metal dichalcogenides (TMDs) belong to one of the most developed types of materials used as solid lubrication. These materials are also extensively used as oil additives or thin films [17]. TMDs are also an important type of self-lubricating materials considered as promising for applications in various branches of science and technology, such as aerospace applications, catalysts, and fuel cells. TMD-based thin films coatings semiconducting structures are also commonly used in photovoltaics as solar energy converters [3] [18] [19].

Tungsten disulfide (WS\textsubscript{2}), which belongs to TMDs family, is an excellent release material for plastic moulds, extrusion dies and other release applications [20]. This material reduces excessive wear, seizing, galling and fretting, as well as improves performance and service life of cutting tools and sliding parts, such as gearbox or bearings. Additionally, WS\textsubscript{2} is a fairly inert and non-toxic material, therefore it has been used in medical device and food processing applications [21] [20].

4.1 Structure of TMDs

Due to a layered structure of TMD films their properties are highly anisotropic [17]. The lamellar crystal structure, similar to that of graphite or talc, is the basis for the excellent lubricating properties and the superlubric state of these materials. TMDs exist in two crystal forms, hexagonal and rhombohedral, however the hexagonal one is of interest for low-friction tribological reduction applications. This is because the hexagonal crystal structure exhibits a lamellar crystal structure [5] [22]. Materials with structures
other than layered 'sandwich' structures can also be used for friction reduction purposes, however they do not offer the same excellent low-friction properties [1].

Transition metal dichalcogenides name indicates that they are made up of transition metals, such as tungsten, molybdenum, cobalt or niobium connected with chalcogens, such as sulphur, tellurium or selenium. TMDs comprise a stacking sequence of layers in which a layer of transition metal atoms is sandwiched between two layers of chalcogen atoms (X-M-X). There are strong covalent bonds between the metal atoms and chalcogenides atoms, while there are only relatively weak Van der Waals forces present between the lattice layer sheets which allows individual sheets to be separated from each other. Within each X-M-X sandwich layer the metal atom (M) is bonded to six chalcogen atoms (X), and each atom of chalcogen sits at the same distance from three metal atoms [2] [22]. An electrostatic coulomb repulsion between the planes giving the material a low shear strength. MoS$_2$, MoSe$_2$, MoTe$_2$, WS$_2$ and WSe$_2$ are the only TMD films that have such structure [5].

Lamellar, low shear strength materials, such as graphite or MoS$_2$, are commonly used as solid lubricants. Shear stresses develop beneath the surface, below the interface between the thin coating and the substrate. The shear stress gradually decreases going toward the surface, and only low shear strength materials are able to fail locally and form debris that will contribute in a transfer layer formation [23].

When sliding of two surfaces in contact takes place in a plane parallel to the TMD layers, weak bonds between the lattice layers are easily broken and low friction sliding is favour. Self-lubricating property of a material is lost in a situation where the crystallites planes are perpendicular to the sliding surface. During self-adaptation of TMDs, strong bonds between the metal atoms and chalcogen atoms are not broken, but layers of cells are moved/rotated and that they are parallel to the substrate. Such alignment of the basal planes means that triboactive coating activates and adapts when exposed to a tribological contact leading to the formation of an easily sheared tribolayer [2] [24].
Tungsten disulfide (WS$_2$) belongs to the transition metal dichalcogenides family and has a type 2H-WS$_2$ layered hexagonal crystal structure where a layer of tungsten atoms is sandwiched between the two layers of sulfur atoms. The schematic diagram of the hexagonal structure of TMDs is shown in Figure 4.2 [25]. During sputtering of WS$_2$, the sheets of WS$_2$ film can grow in different orientations, but they always nucleate in the (001) planes parallel to the substrate. However, for low substrate temperatures and/or high deposition rates, the crystallite orientation changes from (001) to the perpendicular to the substrate (100) leading to a columnar and porous structure. In order to hinder this effect, the substrate can be heated during the deposition what will allow to obtain a denser coating structure [26].

![Figure 4.1: Schematic structure of atomic layers of TMDs [adapted from [25].]](image)

4.2 Fundamental properties of TMDs

Friction

Pure TMDs (e.g. W-S or Mo-S) can be sputtered non-reactively from a compound target or reactively from a metallic target in a presence of reactive gas. The resulting coatings are often substoichiometric with respect to sulfur [1]. Deposited pure
TMD films display excellent tribological properties in vacuum or dry atmosphere (e.g. in dry nitrogen), however they are also known to be highly sensitive to environmental attack, therefore they exhibit number of drawbacks when used as solid lubricants in humid atmosphere [27] [28]. Friction coefficients of 0.035 to 0.05 have been reported in a dry nitrogen environment for sputtered WS$_2$ thin films. In humid air, the friction coefficient increases to 0.4 during the first 1000 cycles of sliding process [29]. Excellent friction properties of TMD coatings can be obtained if there are: an absence of contaminants in the TMD material which can modify the crystal lattice, reorientation of the (002) basal planes of the TMD grains resulting in very low friction between the surfaces in contact, and a formation of a well-adhered TMD tribofilm on the counterpart [22]. Sliding TMD films in ultra-high vacuum conditions can lead to superlubricity where friction and resistance to sliding diminish to nearly zero [27]. Due to a high tendency to transfer, TMD tribolayers quickly form on the counterparts during sliding. These transfer layers have a (002) orientation, which facilitate low-friction sliding due to minimizing the force required for slip and by causing that reactive edges in the planes are not exposed to the air atmosphere, therefore oxidation is hindered [30].

**Hardness and adhesion**

TMD coatings have low adhesion to the substrate, however this can be considerably improved by introduction of a thin metallic interlayer (typically Ti or Cr) between the substrate and the coating [31]. Pure crystalline TMD films produced by PVD technique exhibit very low hardness when compared with competitive low-friction coatings such as diamond-like carbon (DLC). Hardness of TMDs can be significantly increased by doping with a third element [27] [32]. Both low hardness and poor adhesion limit applications of TMD films, particularly when high loading is applied in the contact between the sliding pair [27]. However, increase in hardness is not directly related with decrease in friction resistance of the coating. Prasad et al. [29] have pointed out that if the formation of pores and defects in the structure is prevented, the tribolayer will be less affected by contaminants which may degrade tribological properties of the coating.
Good adhesion of the film to the substrate is promoted by a number of factors, such as: strong atom-atom bonding the interfacial region, absence of easy deformation or fracture modes, no long term degradation modes, loss local stress levels, high fracture toughness of materials, and low concentration of flaws. On the contrary, high residual film stresses, low fracture toughness (brittle materials, flaws), and poor interfacial contact can reduce adhesion. Oxide films and surface contaminants can also cause poor overall adhesion of a film to the surface by giving pinholes in the film. Pores also reduce adhesion due to the fewer bonds at the interface, and because they act as crack initiators [33] [34].

**Oxidation and tribofilm formation**

TMDs are very sensitive to oxidation, therefore reactive species such as O\(_2\) can oxidize these materials to the corresponding oxides (WO\(_3\), MoO\(_3\)) what can diminish their low friction properties [1]. Oxidation of TMDs can take place during sliding against another surface in air environment, specifically when the basal planes are not align parallel to the substrate crystal. The reason for this is that the crystals edges and corners on the (1120) face are more reactive than those of inert (0002) Van der Waals basal planes [2] [35]. There is faster oxidation of the edge planes and moisture penetration through the coating thickness resulting in formation of oxidation products like WO\(_3\) or MoO\(_3\). On the other hand, sliding under a contact load can easily remove the surface oxides and create a pure TMD tribolayer [1] [3]. Furthermore, it has been suggested that the presence of moisture increases the shear strength of TMDs by strengthening the bonds between the sandwich layers, thereby causing higher friction. Zabinski et al. [36], who invesitigated the effect of the environment on W-S-C, observed that the friction coefficient of W-S-C measured in dry air (\(\mu = 0.02\)) is lower than that measured in humid air (\(\mu = 0.15\)). Compared to MoS\(_2\), WS\(_2\) is more resistant to oxidation at high temperature, exhibits higher thermal stability and provides approximately 100\(^\circ\)C increase in maximum operating temperature [37].
Structure

Sensitivity to oxidation as well as very low mechanical strength of TMDs is attributed to their typical columnar morphology when they are deposited in the form of thin coatings (Figure 4.2). Contaminants, such as oxygen or moisture, penetrate porous materials more easily than those with higher density. In the presence of contaminants, the dangling bonds of the crystallites edges can react hindering the sliding process of one lattice layer sheet over another. As a consequence, reorientation of the lattice layers in the contact area is restricted, what leads to worse material lubrication properties. When TMDs are submitted to a shear force, the basal planes slide over one another by intercrystalline slip and transfer to the rubbing counterface [37]. Intercrystalline sliding may also break the covalent bonds and create new dangling bonds resulting in easier degradation of the film [38].

Figure 4.2: SEM micrographs of columnar sputtered WS$_2$ film [38].

Crystalline coatings are usually divided into two categories depending on the orientation of the basal planes. Coatings with the basal planes perpendicular to the surface and the $c$ axis parallel to it (type I orientation) consist of loosely packed standing flakes and often exhibit columnar structure. A type II orientation has basal planes parallel to the surface and the $c$ axis perpendicular to it. This type of orientation is beneficial for tribological and electrical properties of material [1].

One way to improve the microstructure as well as tribological and mechanical properties of TMD coatings is to dope them with other elements [2].
4.3 TMD-based coatings

Different types of coatings microstructure are schematically shown in Figure 4.3 [22]. MoS$_2$ and WS$_2$ films are the most studied among TMD coatings [28]. As mentioned above, pure TMD coatings have usually columnar morphology with high porosity, very low hardness, low adhesion to the substrate, and limited tribological performance in the presence of humid air [3]. Improvement of mechanical and tribological properties, as well as densification of pure TMD films can be achieved by doping with a third element. The dopant element introduced in the deposition process of TMDs allows to avoid formation of large grains and defects in the films, as well as hinders growth of the columnar structure [2]. In some cases, the resulting structure is fully amorphous [3] what lessen the chance of failure attributable to the columnar structure and, consequently, give better protection against contaminants [2]. Moreover, an addition of the third element to the TMD system leads to denser and harder coating [30].

![Figure 4.3: Schematic representation of W-S-C coating design: (a) nanocomposite coatings with hard WC nanoparticles embedded with WS$_2$ nanograins in an amorphous C-matrix, (b) nanograins of WS$_2$ in a C-matrix, (c) super-lattice WS$_2$+C layers film [22].](attachment:image)

Studies on doping TMDs with carbon started in late 90’ due to idea of Voevodin et al. [36] of nanocomposite structure coatings to combine nanocrystals of self-lubricant WS2 and hard WC phases embedded into amorphous carbon matrix. Cavaleiro et al. [39] presented similar concept for deposited by magnetron sputtering WS$_2$ coatings doped with C or N. Doped films showed improvement of hardness and wear resistance, with the best mechanical properties obtained for addition of around 50 at.% of C or N. It has been also observed that WS$_2$ film doped with carbon does not fail rapidly as it can be typically seen in case of pure WS$_2$ [24]. Another concept for the TMD coatings doped with carbon deals with alternately placed nanolayers of WS$_2$ and C forming a super-lattice film [22].
Chapter 5

Thin films

For more than a half century thin films have been used for manufacturing optical, electronic and mechanical devices, instrument hard coatings and decorative parts. In 1960s, thin film technology was widely used in the optical industry and manufacturing of semiconductors. Since then thin films processing techniques have developed significantly and a variety of functional materials have been formed [40]. Thin film is a traditional and well-established technology in material science and one of the key processing of new materials, such as nanomaterials or man-made superlattices [41].

5.1 Basic aspects of thin films

Some film properties, such as crystal phase and orientation, composition, thickness, and microstructure, can be controlled during the deposition process. Thus, thin films possess some novel properties like quantum size effects, crystalline orientation or multilayer aspects that cannot be found in bulk materials [41].

There are many deposition methods for material formation, however not all can be used for thin films deposition. Thin film technology involves deposition of one-by-one source material molecules, atoms or ions on a substrate [40]. Thin film is defined as a layer of material which has thicknesses in range from several micrometres or less (1 μm = 10^{-6} m) down to a few nanometres (1 nm = 10^{-9} m) [42]. Thinner coatings could enable surface asperities to break through the coating, causing metal-metal contact, and consequently increasing the friction. On the other hand, using thicker coatings increase friction because such coatings are subjected to ploughing, and they more easily get adhesive failure which
results in removal of large parts of the film [5]. The properties of thin films are often affected by the substrate on which thin films are deposited, and can vary considerably through the film thickness [43].

5.2 Thin film nucleation and growth process

Growth of the single film layer on a substrate in an atom-to-atom deposition process is shown in Figure 5.1 [44]. Atoms evaporated from the source material are transported through a medium (i.e. argon) to the substrate. Some of atoms are adsorbed on a growing surface of the substrate either directly or through a chemical or electrochemical reaction [44]. The adsorbed species are not in thermal equilibrium with the substrate, therefore they move over the substrate surface, interact among themselves and form bigger clusters also known as critical nuclei. Nuclei can either desorb or collide with other absorbed species consequently growing in size and forming so-called islands. In the next stage of the film formation process the small islands start combining with each other in order to reduce the substrate surface area and form a solid, continuous film [41].

![Figure 5.1: Growth mechanism of thin films [25].](image)

Materials deposited on foreign substrate can grow in different ways. Schematic representation of thin film growth modes are shown in Figure 5.2. Three main modes of thin films growth are the following [45]:

1. Evaporated atoms
2. Adsorbed on substrate
3. Brownian motion
4. Trapped atoms
5. Nucleation & film growth
• layer-by-layer mode which correspond to the situation when film atoms are bound more strongly to the substrate than to each other. As a result, the 2D film is form which covers the substrate uniformly;

• island mode which refers to the case when film atoms are more strongly bound to each other than to the substrate resulting in 3D islands nucleate and growth directly on the substrate surface;

• layer-plus-island mode which is an intermediate case between island and layer growth and represents the situation when after the growth of 2D layer, the growth of 3D islands takes place.

![Figure 5.2: Schematic representation of thin film growth modes: (a) layer-by-layer, (b) island, (c) laser-plus-islands [45].](image)

### 5.3 Thin films deposition techniques

During the last many decades the thin films manufacturing techniques have improved considerably [46]. There are several deposition techniques available for material formation. The thin film deposition process is typically classified into two systems: the chemical vapour deposition (CVD) and physical vapour deposition (PVD) which is divided into thermal evaporation and sputtering [40]. PVD technique of magnetron sputtering is explained as this technique has been employed in thin films deposition in the present thesis work.
5.3.1 Physical vapour deposition (PVD)

Physical vapour deposition (PVD) processes are atomistic deposition processes in which raw material of the film is evaporated from the target in form of atomic/molecular/ionic species by heating it with high energy electron beam or by using thermally heated filament. The evaporated material is transported through vacuum/low pressure gas/plasma to the substrate where condenses [43].

Typically, PVD technique is used to produce thin layers of materials on the substrate, however it can also be used to fabricate thick deposits, graded composition deposits or multilayer coatings. PVD can be also used to deposit films of elements and alloys as well as compounds when reactive deposition processes are employed [43].

There are several PVD techniques for fabricating coatings in a vacuum conditions and they can be divided into two groups: (i) thermal evaporation, where raw material of the film is heated in vacuum until its vapour pressure reaches values greater than that of the ambient pressure, and (ii) sputtering methods [47]. Number of sputtering systems are used in practice for materials deposition including direct current (DC) sputtering, radio frequency (RF) sputtering, arc evaporation, ion-beam sputtering and, high power impulse magnetron sputtering (HiPIMS), magnetron sputtering or pulsed laser deposition (PLD)[46]. The focus here is given to the DC magnetron sputtering as these technique has been used to deposit thin film in the present thesis work.
Chapter 6

Sputtering

Sputtering is a PVD process for depositing films of materials onto a substrate by ejecting atoms from the source of the material to be deposited (sputtering target) by high energy ion bombardment in a high vacuum environment using either an ion gun or low pressure plasma. Particles ejected from the vaporization source (target) travel toward the substrate onto which they condense and form atomic film layers [43].

Plasma or glow discharge is required in order to perform sputtering process. Plasma can be form by using either direct current or radio frequency power. DC power is used to sputter electrically conductive materials, while RF power can be apply for depositing electrically insulating materials, like oxides of aluminium, silicon, etc. [40]. It is also possible to deposit oxides or nitrides by allowing the metal to react (reactive sputtering) with a gaseous phase (oxygen or nitrogen, respectively) or carbides. However, all these processes have rather low deposition rates. In order to achieve higher deposition rates, magnetron-type discharge technique can employed [48] [43].

Increasing the deposition rates can be done by lowering the gas pressure in the deposition chamber because it provides a longer mean free path for atom-gas collision during travelling between the target and the substrate. Ejected atoms must be able to travel freely towards the substrate with as little as possible collisions with another gas atom. Above pressures of 1 Pa, atoms undergo many collisions and this could cause drop in the deposition rates. Besides increasing the deposition rates, low pressure gaseous environment is also required in order to maintain high ion energies, as well as to control the amount of gaseous and vapour contamination in the chamber [47] [43].
Deposition of coatings can take place from elemental or compound targets. Deposition of compounds with controlled composition is possible by sputtering two different target materials, with the power to each of the targets controlled independently (co-sputtering). Co-sputtering process can be also performed in the presence of a reactive gas, such as oxygen or nitrogen [49], as well as with magnetron or ion-beam source. It is also possible to apply a bias to the substrate in order to enhance reactivity at and surface [47] and consequently induce ion bombardment, however this technique causes stresses in the coating, as well as re-sputtering of the deposited material off the film and consequently reduction of the deposition rate [50].

6.1 Direct current sputtering

DC diode discharge is the simplest system for forming a plasma. The DC sputtering system consists of two planar electrodes within a vacuum chamber and an external high-voltage power supply. One of electrodes is cathode covered by target material to be deposited, and the other electrode is anode onto which substrates are placed. Prior the deposition process, an inert gas, typically argon, is introduced into a vacuum chamber. Under appropriate conditions of gas pressure and applied voltage between electrodes, the gas will breakdown into a plasma discharge [42]. The glow discharge is present between electrodes under voltage. An inert gas ions formed in the glow discharge are accelerated in a direction of the target and sputter the target surface. This results in the ejection of target atoms and further deposition of the target material on the substrate in form of thin films [40] [50].

6.2 Magnetron sputtering

Although the basic sputtering has been known for years, this process turned to be unsuitable for many industrial applications due to its low deposition rates, high substrate heating effect and low plasma ionisation efficiency [51]. Sputtering was first
observed by Grove in 1852 and Plücker (1858). The invention of magnetically enhanced variant of sputtering (known as magnetron sputtering) which derives from the work of Kesaev and Pashkova (1959) in confining arcs and Chapin (1974) in developing the planar magnetron sputtering source, marked the beginning of new vacuum coating technology. Since then, magnetron sputtering has developed rapidly and now is used in a wide range of industrial branches needing high quality coatings [52] [53] [43]. Applications of magnetron sputtering process include low friction coatings, hard, wear-resistant coatings, corrosion resistant coatings, decorative coatings and coatings with specific electrical, or optical properties [52].

Magnetron sputtering is used to deposit coatings with thicknesses up to about 5 μm. This techniques uses the principle of applying a specially shaped magnetic field to a diode sputtering target. The magnetic field traps electrons a region close to the cathode resulting in more efficient ionisation as, in this configuration, an ionising collision of electrons with a gas atom is increased [47]. Application of a magnetic field allows the electrons to circulate in a circular path around the target increasing plasma density and therefore the deposition rate [48]. When impedance of a plasma drops, the magnetron source operates at much lower voltages than diode systems (500-600 V as compared with several kV) [47]. Scheme of the magnetron sputtering process is shown in Figure 6.1. The primary advantages of magnetron sputtering include [47] [53]:

- low plasma impedance and therefore high discharge currents,
- deposition rates in the range from 1 nm/s to 10 nm/s, excellent uniformity of on large-area substrates coatings,
- highly pure and dense coatings, excellent coverage of steps and small features, ease of automation.

Required coating composition is not always possible to obtain by sputtering from one or multiply targets. This problem can be solved by introducing a reactive gas to the sputtering chamber (reactive magnetron sputtering) [47]. An example is when nitrogen is introduced to the process of sputtering from a tungsten disulfide target in order to form
Figure 6.1: A magnetron sputtering system during co-sputtering process from two targets [1].

W-S-N film. The composition of the growing film can be controlled by controlling the reactive gas flow rate. Reactive sputtering might lead to the formation of the compound on the surface of the target, namely to target poisoning [47].
Chapter 7

Experimental procedure

The objective of this thesis was to study structure and composition of low friction transition metal dichalcogenides coatings in contact with rubber, as well as to understand the effect of nitrogen on their mechanical properties and tribological performance at varied temperatures. The coatings composition was varied by changing the flow of \( \text{N}_2 \) into the deposition chamber, leading to N contents ranging from 0 to 32.64 at.%. Five W-S(-N) coatings with different nitrogen content were deposited by DC magnetron sputtering. Produced coatings were characterized concerning their chemical composition, mechanical and tribological behaviour, structure, morphology and adhesion using the following techniques: WDS, nanoindentation, ball-on-disc, XRD, SEM and scratch test.

7.1 Deposition procedure

The W-S and W-S-N coatings were deposited in a vacuum chamber from \( \text{WS}_2 \) and Cr targets using UDP 650 Teer Coatings deposition equipment (Teer Coating Limited). Prior the depositions, the steel substrates were polished with a diamond paste of particle size down to 3 μm in order to obtain better tribological performance and coating adhesion. Steel substrates were also ultrasonically cleaned in acetone and alcohol in order to remove undesirable contaminants from the surface. The substrates were mounted in a rotating substrate holder (10 rev/min). Prior the depositions, the chamber was pumped down to \( 10^{-4} \) Pa. Inside the chamber, the substrate and the targets were cleaned simultaneously in an argon atmosphere for 40 min by establishing the plasma close to the substrates electrode with a voltage of 600 V on the substrate. The same Ar flow
(50 at.% Ar) was used in all depositions. Values of used total discharge pressure and the partial pressure of N\textsubscript{2} are given in Table 7.1. A total of five depositions with different nitrogen partial pressure were made. A chromium interlayer (∼300-360 nm) was deposited on the substrates in order to improve adhesion of the top film to the substrate.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Partial pressure of N\textsubscript{2} [Pa]</th>
<th>Total Ar + N\textsubscript{2} discharge pressure [Pa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-S</td>
<td>0</td>
<td>0.35</td>
</tr>
<tr>
<td>W-S-N2.5</td>
<td>0.08</td>
<td>0.37</td>
</tr>
<tr>
<td>W-S-N5</td>
<td>0.15</td>
<td>0.39</td>
</tr>
<tr>
<td>W-S-N10</td>
<td>0.24</td>
<td>0.42</td>
</tr>
<tr>
<td>W-S-N20</td>
<td>0.35</td>
<td>0.49</td>
</tr>
</tbody>
</table>

### 7.2 Materials and coatings

The coatings were deposited on silicon wafers (for mechanical and analytical testing) and on AISI 52100 100Cr6 steel substrates (for adhesion and tribological purposes). Steel substrate were disc-shaped type with size Ø50x5 mm. Type 100Cr6 is a low alloy martensitic chrome steel widely used to manufacture mechanical components due to its high hardness, wear resistance, surface finishing and dimensional precision. Chemical composition of type 100Cr6 steel is presented in Table 7.2 [54].

In order to investigate influence of nitrogen on the thermo-mechanical and tribological behavior of TMD coatings, five different W-S based films were deposited: W-S (as a reference), W-S-N2.5, W-S-N5, W-S-N10, W-S-N20 (numbers correspond to the % of nitrogen flow, where 0% stands for a closed flowmeter, and 100% stands for a completely open flowmeter). Coatings were tribologically tested at two different temperatures of ∼25°C (RT) and 200°C at humidity of ∼45%. An industrial grade acrylonitrile butadiene rubber (NBR) balls with diameter d = 10 mm were used as a counterbody in a pin-on-disc experiment. Conditions of the tribological testing are described below.
Table 7.2: Typical chemical composition of type 100Cr6 steel, wt.% [54].

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>100Cr6</td>
<td>0.93-1.05</td>
<td>0.15-0.35</td>
<td>0.25-0.45</td>
<td>max. 0.025</td>
<td>max. 0.015</td>
<td>1.35-1.60</td>
<td>max. 0.10</td>
</tr>
</tbody>
</table>

7.3 Characterisation techniques

Various test equipment was used for coatings characterisation. The chemical composition was evaluated by wavelength dispersive spectroscopy (WDS). The thickness of the films was measured by using scanning electron microscopy (SEM). Surface and fractured cross section morphologies of the coatings were examined with SEM equipped with energy dispersive analysis of X-ray (EDX) with an acceleration voltage of 15 kV.

The crystallographic structure of coatings was investigated by X-ray (XRD). The XRD measurements were carried out in Philips X-Pert Pro MPD diffractometer using Cu Kα radiation (λ = 0.154 nm) in conventional (Θ - 2Θ) mode. Further, grazing incidence x-ray diffraction (GIXRD) was carried out using a grazing incidence angle of 2°. In conventional scanning Θ - 2Θ method the beam penetration depth may be greater than the thin film thickness. The Θ - 2Θ mode generally produces weak signals from the coating and intense signal from the substrate. Therefore, in case of thin films it is convenient to use the X-ray diffraction at the grazing incidence (GI-XRD) in order to minimize the effect of the substrate. The GI-XRD mode uses the small and constant incident angle (1° - 3°) which results in scattering at small depth [55]. XRD analyses were performed on the coatings deposited onto Si-wafer substrates.

The adhesion scratch test allows to determine how strong a coating adheres to the substrate, and to obtain the critical load that are related to adhesion properties of coatings. The adhesion of the coatings was evaluated in CSEM Revetest scratch testing equipment using a sphero-conical diamond stylus with a tip radius 0.2 mm. The stylus was drawn across the sample at a constant speed of 10 mm/min, loading rate of 100 N/min, and at progressive load. The normal load was increasing linearly from 5 N up to 50 N.
as the indented moved across the test surface at a constant speed. A maximum load was limited to 50 N to prevent unnecessary wear of the stylus. Loaded stylus results in stresses at the coating/substrate interface which cause a well-defined failure event at so-called the critical load [56]. The critical load \( L_c \) (the smallest load at which failure appears) data was used to quantify the adhesive properties of the films. The critical load values were obtained by analysing the failures events in the scratch track by optical microscopy using Leica DM4000 M LED microscope. Figure 7.1 shows a schematic diagram of the adhesion tester used for testing.

![Schematic diagram of the scratch test](image)

**Figure 7.1:** Schematic diagram of the scratch test (not to scale) (adapted from [57]).

**Nanoindentation** is a technique used to measure hardness of a material at very shallow depth, so that minimal influence from the substrate is achieved [5]. NanoTech Nanointerder (Micro-Materials Ltd.) Nanoindentation equipment equipped with a Berkovich diamond pyramid indenter was used to determine hardness and Youngs modulus of the coatings. Hardness, \( H \), which is resistance of material to plastic deformation caused by indentation, was calculated from by equation (7.1), where \( F_{\text{max}} \) is the maximum load applied during the indentation, and \( A_c \) is the contact area of the indentation immediately before unloading.

\[
H = \frac{F_{\text{max}}}{A_c} \quad (7.1)
\]
When the load is applied to the intender, the depth of indentation beneath the surface of the specimen is measured. The geometry of the indenter allows the size of the contact area to be determined [58] [59].

Depth-sensing nanoindentation testing was performed on coatings deposited on steel substrate. The mechanical properties of each coating were evaluated as the average of 32 different measurements (16 indentations made in two different zones of the sample). The measurements were carried out on the free surface of each of the samples. The measurements were performed at ambient temperature (∼23°C). A maximum applied load of 5.06 mN was set in order to keep the hardness measurement independent on substrate. The nanoindentation load vs/ displacement curves presented in Appendix in Figure A.1 show that the indentation depth is ∼10-15% of the coating thickness for W-S-N films and ∼27% for W-S coating. The experiments were carried out using the loading/unloading rate of 0.17 mN/s and a holding time at maximum load of 30 s to saturate creep effect before unloading.

The tribological behaviour of the films was evaluated using a pin-on-disc rotational tribometer. The friction coefficient measurement setup and the schematic representation of the contact in the pin-on-disc setup used in the present work is shown in Figure 7.2.

![Figure 7.2: The friction coefficient measurement setup with the heating apparatus (a) and the schematic representation of the contact in the rig (b).](image)
Coatings for tribological purpose were deposited on a disc-shaped steel substrate. Tests were performed in air with a relative humidity of ∼45% and at two temperatures: ambient temperature (∼23°C) and elevated temperature (200°C). Two measurements of 5 000 sliding cycles and 50 000 sliding cycles were performed for each sample. A rotating disc (diameter ⊙ = 50 mm; height h = 5 mm) slid against a stationary rubber ball (diameter ⊙ = 10 mm) with the constant speed of 0.1 m/s. A new ball was used in each test and one disc-shaped sample was used to perform two tests with different number of laps. The ball was loaded with 5 N (0.5 kg). During the tests, the friction coefficient was measured. The reported friction coefficient is the average value of the steady state. In cases when the steady state was not obtained, the reported friction coefficient is the average value of the whole test. The friction coefficient is given by equation (7.2) where F is a friction force, and N is the normal load [2]. Chemical composition of the wear tracks and the ball wear scars was determined by EDS (energy dispersive spectroscopy) analysis.

\[ \mu = \frac{F}{N} \] (7.2)

The wear rate (k) was determined using a 2D surface profilometer (Mahr Perthometer S4P) by measuring the profile across the wear track and then calculating the sectional area removed. This value was multiplied by the wear track circumference and the sliding distance, then the volume of material removed was calculated, and the wear rate was found (mm³N⁻¹m⁻¹). The wear rates were calculated through the equation (7.3) where V is a wear volume, S is a total running distance of the ball over the disc, and N is the normal applied load. The wear volume of each coating and test conditions was evaluated as the average of three measurements made in three different zones of the wear track.

\[ k = \frac{V}{S \times N} \] (7.3)
Chapter 8

Results and discussion

8.1 Chemical composition

Elemental chemical composition of the coatings determined by WDS analysis, and their total thickness obtained by SEM are shown in Table 8.1. W-S thin films were deposited with different N contents in the range 0 - 32.64 at.% by varying the nitrogen partial pressure in the deposition chamber. Nitrogen content and S/W ratio as a function of the partial pressure are presented in Figure 8.1. As it was expected, there is more nitrogen present in the films with an increase of N\textsubscript{2} partial pressure. Moreover, there is no relation between the S/W ratio and content of N. The thickness of the W-S-N coatings is in the range between 1.1 and 1.8 μm, however for W-S film the thickness is higher (2.9 μm) what can be related with less compacted structure of this material. All coatings consists of an approximately 0.30-0.36 μm chromium interlayer.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Total pressure [Pa]</th>
<th>Chemical composition [at.%]</th>
<th>S/W ratio</th>
<th>Thickness [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>W</td>
<td>S</td>
<td>N</td>
</tr>
<tr>
<td>W-S</td>
<td>0.35</td>
<td>32.18</td>
<td>56.54</td>
<td>0.00</td>
</tr>
<tr>
<td>W-S-N2.5</td>
<td>0.37</td>
<td>38.66</td>
<td>46.85</td>
<td>6.85</td>
</tr>
<tr>
<td>W-S-N5</td>
<td>0.39</td>
<td>32.88</td>
<td>45.63</td>
<td>15.60</td>
</tr>
<tr>
<td>W-S-N10</td>
<td>0.42</td>
<td>27.68</td>
<td>38.88</td>
<td>23.18</td>
</tr>
<tr>
<td>W-S-N20</td>
<td>0.49</td>
<td>26.82</td>
<td>32.24</td>
<td>32.64</td>
</tr>
</tbody>
</table>

Elemental chemical composition of coatings was normalized to 100 at.% of tungsten (W), sulphur (S) and nitrogen (N). Besides these elements, oxygen and carbon
were detected, however, regarding the deposition methods and the types of deposited material, the contaminants content can be consider as normal. The carbon concentration ranges from around 3 at.% to 8 at.% and is thought to origin from impurity of the target due to its contamination during manufacturing or usage together in the deposition of coatings containing carbon. The oxygen presence in the sputtered coatings, as other researchers have pointed out [60], may come from the residual water vapour in the deposition chamber. Although the vacuum pressure reached before deposition was as low as $10^{-5}$ Pa, sputtering of elements (i.e. W) with strong affinity for oxygen can give a rise to incorporation of oxygen in the deposited coating, and can reach values greater than 10 at.% [39]. In general, W-S films are less compacted than the doped ones what results in more likely adsorption of contaminants [28]. However, in this study the oxygen content in W-S film is not higher than in doped coatings. This is presumably due to the aforementioned residual atmosphere of the deposition chamber and the deposition rate. At slower deposition rates the concentration of oxygen in the film will be higher [61].

The S/W ratio varies in the range 1.2 - 1.76, with the highest value for undoped coating. Deposited coatings exhibit a sulfur deficiency in relation to W-S stoichiometry what could be related with formation of volatile S compounds or with the resputtering of S from the substrate promoted by the Ar neutrals. Mutafov et al. [28] reported that sulfur deficiency is a common feature of these type of coatings, as well as that during ion bombardment of a compound material, the element with lower atomic mass (S) is more likely to be ejected from the substrate than the heavier one (W).
Figure 8.1: Evolution of the S/W ratio and nitrogen content in the coatings as a function of increasing partial pressure of nitrogen.

8.2 Morphology and structure

XRD

XRD diffractograms of tested coatings deposited with increasing partial pressure of nitrogen are shown in Figure 8.2. Different peak positions, intensities and broadening are observed depending on the nitrogen content. As can be seen from this figure, only W-S film and the film with the lowest N content (W-S-N 2.5) present crystalline peaks related to the WS$_2$ structure. As reported by Nossa et al. [62], W-S films show the WS$_2$ hexagonal phase preferentially oriented following (100) plane. In case of W-S, there are three main asymmetric peaks at $2\Theta = 33.38^\circ$, $59.14^\circ$ and $69.86^\circ$ which can be assigned to the (100), (110) and (108) planes, respectively. This pattern is typical of sputtered WS$_x$. The long shoulder on the right side of the asymmetrical peak indexed as (100) corresponds to a turbostractic stacking of S-W-S single layers giving rise to a series of planes of type (10L) (L=1, 2, 3) [60]. The reason of the asymmetry is a turbostratic stacking, which means that the basal planes are rotated relative to each other [63]. The broad peak observed at $2\Theta = 14^\circ$ indicates the beginning of the basal planes formation as reported by Regula et al. [60].
Doping W-S film with N results in broadening of the (100) peak, indicating change in crystallinity size of the WS$_x$ phase [63]. W-S-N2.5 coating shows a prominent orientation of the (002) basal plane of the hexagonal WS$_2$ phase with the main diffraction peaks placed at $2\Theta = 13.5^\circ$. As can be seen from Figure 8.2, with further increase in N content, the diffractions peaks become blunter and decreased in intensity, suggesting change in crystallinity size. These results agrees with the work of Nossa et al. [39] who observed change is crystallinity size with addition of N/C to W-S films. For coatings W-S-N5, W-S-N10 and W-S-N20, it is not possible to detect any crystalline feature in the XRD pattern, suggesting the existence of an amorphous structure [64]. The broad features observed for the amorphous coatings are not possible to assign to any specific phase.

**Morphology**

Scanning electron micrographs of fractured cross sections (Figure 8.3) show a change in coatings morphology with the addition of nitrogen. The undoped W-S film has

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**Figure 8.2:** X-ray diffractograms for a series of W-S(-N) coatings with increasing N content.
columnar morphology (Figure 8.3(a)), what is a typical feature of WS\textsubscript{x} coatings deposited by sputtering from WS\textsubscript{2} target, as reported previously by Nossa et al. [38].

![Cross-sectional SEM micrographs of W-S and W-S-N sputtered films deposited with increasing N content: (a) W-S, (b) W-S-N2.5, (c) W-S-N5, (d) W-S-N10, (e) W-S-N20.](image)

**Figure 8.3:** Cross-sectional SEM micrographs of W-S and W-S-N sputtered films deposited with increasing N content: (a) W-S, (b) W-S-N2.5, (c) W-S-N5, (d) W-S-N10, (e) W-S-N20.

A columnar type microstructure results from surface roughness and geometric shadowing which lead to preferential growth of elevated regions [33]. The incorporation of N for W-S-N films deposited in reactive nitrogen atmosphere results in compactness of the columnar cross sections morphologies. SEM micrographs of the W-S(-N) sputtered
films, deposited with increasing partial pressure of N are presented in Figure 8.4. As can be seen, the surface morphologies seems to be smoother for more compacted W-S-N coatings. This results agree with research of Nossa et al. [38] on the effect of a third element on morphology of doped TMD films.

![Surface morphology of W-S and W-S-N sputtered films deposited with increasing N content: (a) W-S, (b) W-S-N2.5, (c) W-S-N5, (d) W-S-N10, (e) W-S-N20.](image-url)

**Figure 8.4:** Surface morphology of W-S and W-S-N sputtered films deposited with increasing N content: (a) W-S, (b) W-S-N2.5, (c) W-S-N5, (d) W-S-N10, (e) W-S-N20.
8.3 Adhesion

Good adhesion is a fundamental requirement of any film-substrate system [33]. Adhesion of a coating to the underlying substrate is a critical property for the coating durability. Adhesive strength determines the film’s endurance life and load bearing capacity. Therefore, the coating needs to firmly attach to the substrate. If the coating even partially becomes delaminated from its substrate, it no longer fulfils its purpose. For a coating to be retained and to perform its function, its adhesion to the substrate must tolerate mechanical and thermal stresses, elastoplastic distortions, and environment impact, i.e. impact of moisture [65].

Optical micrographs of scratch tested specimens are presented in Figure 8.5. According to Figure 8.5, the failure mechanisms observed for the tested coatings can be characterised by an initial part of insignificant plastic deformation followed, in some cases, by interfacial spallation at the border of the scratch track, local spallation inside of the scratch track, or longitudinal cracks at the borders of the scratch track [66]. The microscopic observation of the scratches revealed failure events, which are identify and labelled as $L_{C2}$ and $L_{C3}$. As reported by Sinha [67], $L_{C2}$ stands for first adhesive chipping at track edges, while $L_{C3}$ coating delamination within the track or large area coating chipping. Critical loads values for tested coatings are shown in Table 8.2.

W-S film (Figure 8.5(b)) exhibits substrate exposure at low load of 11 N. Coatings W-S-N10 (Figure 8.5(h)) and W-S-N20 (Figure 8.5(j)) do not show any damage neither in the scratch sides nor into the scratch path, however there are longitudinal cracks at the borders of the scratch track present at 36 N and 41 N applied load, respectively. On the other hand, coating W-S-N2.5 (Figure 8.5(d)) exhibited local spallation inside of the scratch track at the $L_{C2}$ value of 27 N, and interfacial spallation at the border of the scratch track starting at 33 N. Interfacial spallation at the border of the scratch track can be also observed for W-S-N5 coating (Figure 8.5(f)) at $L_{C2}$ value of 44 N.

Initial failure of W-S and W-S-N2.5 films below applied load of 50 N could be related with their crystalline structure. On the contrary, coatings W-S-N5, W-S-N10
and W-S-N20, which are amorphous, does not fail throughout the test and exhibit the \(L_{C3}\) values above 50 N. These results agrees with study of Gustavsson [5] who reported that by doping TMD films, the microstructure is often changed, in many cases resulting in completely amorphous structure which is more compacted and have higher adhesion strength. In addition, no delaminated zones of the coating from the substrate can be observed even for the highest applied loads. For this reason, adhesion of the coatings was considered to be sufficient for further tribological testing under load of 5 N.

**Table 8.2:** Critical loads of scratch test.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Failure modes [N]</th>
<th>(L_{C2})</th>
<th>(L_{C3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-S</td>
<td>N/A</td>
<td>27</td>
<td>33</td>
</tr>
<tr>
<td>W-S-N2.5</td>
<td></td>
<td>44</td>
<td>N/A</td>
</tr>
<tr>
<td>W-S-N5</td>
<td></td>
<td>36</td>
<td>N/A</td>
</tr>
<tr>
<td>W-S-N10</td>
<td></td>
<td>41</td>
<td>N/A</td>
</tr>
<tr>
<td>W-S-N20</td>
<td></td>
<td>41</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Figure 8.5: Optical micrograph of the scratch (10x magnification) and of the final part of scratch (20x magnification) for coatings in as deposited condition: (a)(b) W-S, (c)(d) W-S-N2.5, (e)(f) W-S-N5, (g)(h) W-S-N10, (i)(j) W-S-N20.
8.4 Mechanical properties

Mechanical properties of studied coatings evaluated by depth-sensing nanoindentation technique are presented in Table 8.3. The hardness (H) and reduced Young’s modulus (E) of studies coatings as a function of nitrogen content are shown in Figure 8.6.

Coatings deposited with nitrogen show a significant increase in the hardness, in relation to an undoped film. The properties of the W-S-N films do not vary with the concentration of N. All W-S-N films show similar hardness values equal approximately 6 GP. Hardness of W-S-N coatings is more than one order of magnitude higher than values obtained for an undoped film (0.34 GPa). Obtained results are very promising and are in good agreement with work of Nossa et al. [31] who reported significant improvements in the hardness (from 0.6 GPa to 6 GPa) when W-S film was doped with N. Young’s modulus (E) follows approximately the same trend as hardness. There are several factors which can contribute to higher hardness and elastic modulus of the doped coatings, such as an increase in structure compactness resulted from doping W-S film with N.

![Figure 8.6: Hardness and reduced Young's modulus of W-S and W-S-N coatings as a function of nitrogen content.](image-url)
Table 8.3: Mechanical properties and critical load of W-S and W-S-N coatings.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Hardness [GPa]</th>
<th>Hardness error [GPa]</th>
<th>Reduced Young’s modulus [GPa]</th>
<th>Reduced modulus error [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-S</td>
<td>0.34</td>
<td>±0.02</td>
<td>23.80</td>
<td>±0.95</td>
</tr>
<tr>
<td>W-S-N2.5</td>
<td>6.30</td>
<td>±0.46</td>
<td>100.45</td>
<td>±3.9</td>
</tr>
<tr>
<td>W-S-N5</td>
<td>6.13</td>
<td>±0.61</td>
<td>110.70</td>
<td>±8.25</td>
</tr>
<tr>
<td>W-S-N10</td>
<td>5.48</td>
<td>±0.30</td>
<td>108.75</td>
<td>±4.25</td>
</tr>
<tr>
<td>W-S-N20</td>
<td>5.54</td>
<td>±0.14</td>
<td>98.00</td>
<td>±2.8</td>
</tr>
</tbody>
</table>

8.5 Tribological behaviour

The pin-on-disc tests were performed for W-S and W-S-N coatings during the 5 000 (5k) and 50 000 (50k) sliding cycles. Results were obtained at room temperature and at 200°C.

Tribological behaviour at room temperature

The reported friction coefficient is the average value of the whole test as the coefficient of friction (CoF) did not achieve the steady-state. The average CoF obtained during the pin-on-disc tribological testing at room temperature is shown in Figure 8.7. As can be seen from the figure, all W-S-N coatings tested for 50k laps have the CoF in the range from ~0.6 to ~0.9. These values are very close to that obtained for the uncoated steel (μ=0.59). This could possibly be due to the coatings removal or partial removal at the contact area with the ball counterpart. On the contrary, W-S film has lower the average CoF (μ=0.38) what could be possibly caused by formation of a tribofilm. In order to understand tribological behaviour of tested materials, surface profilometry of the wear tracks, EDS chemical analysis in the wear tracks (Figure 8.8) and on the ball wear scars, as well as microscopic observations were performed.

2D profilometry of coatings after the tribological test provides information regarding the depth of the wear tracks. Obtained results were further used in order
to calculate the coatings wear rates (not presented). Comparison of wear tracks depth after 50k laps tests and the thickness of corresponding as-deposited coatings shows that the wear tracks depth is equal or greater than thickness of the as-deposited coatings. On the contrary, the wear tracks depth was lower than the coatings thickness after the 5k laps tests, with the exception of the softer W-S film. Moreover, wear rates (not presented) are high for all coatings. Further EDS analysis in the wear tracks (Figure 8.8 (a), Figure 8.8 (b)) and of the powdery worn particles formed near the wear track area after the 50k laps tests (Figure 8.8 (c)) reveals presence of the coating material, Fe and Cr, indicating that the chromium interlayer and the substrate were reached. These results confirm the assumption that the coatings were partially removed during the tribo-test. Comparison of the EDS analysis of the as-deposited coatings (see Table 8.1) and the material in the wear tracks formed after tests at room temperature was made in order to evaluate the difference in the chemical composition. The comparison shows that, in general, there is less W, S, and N, as well as more C and O present in the material of the wear tracks. However, more in-depth experiments should be performed to understand the nature of these differences.

In order to investigate whether the that lower CoF of W-S film is due to the formation of a functioning tribofilm, EDS analysis and microscopic observation of the ball wear scars were performed. W-S coating maintains low friction despite almost
Table 8.4: Comparison of coatings thickness and coatings wear tracks depth after 5 000 and 50 000k laps tests at room temperature.

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>at. %</th>
<th>Number of sliding cycles</th>
<th>Wear track profile depth [μm]</th>
<th>Coating thickness (without Cr interlayer) [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5 000</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 000</td>
<td>2.4</td>
<td>2.5</td>
</tr>
<tr>
<td>W-S</td>
<td></td>
<td>5 000</td>
<td>0.7</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 000</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>W-S-N2.5</td>
<td></td>
<td>5 000</td>
<td>0.35</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 000</td>
<td>1.4</td>
<td>1.6</td>
</tr>
<tr>
<td>W-S-N5</td>
<td></td>
<td>5 000</td>
<td>0.45</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 000</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>W-S-N10</td>
<td></td>
<td>5 000</td>
<td>0.8</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 000</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>W-S-N20</td>
<td></td>
<td>5 000</td>
<td>0.8</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 000</td>
<td>1.4</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Figure 8.8: Chemical composition of the selected wear tracks obtained by EDS after testing at room temperature: (a) W-S, 5k laps, (b) W-S-N10, 50k laps, (c) powdery worn particles, W-S-N2.5, 50k laps.

Micrographs of the ball wear scars produced during 50k laps tribological tests at room temperature are presented in Figure 8.10. Micrographs of the the ball wear scars produced during the 5k laps test are not presented as they show similar features compared to the 50k laps tests.

Complete removal of the coatings material. It is worth pointing out that for this type of material, coating failure is not necessarily associated with abruptly increased friction. It has previously been observed that the presence of a tribofilm may be sufficient to maintain low friction even when most of the original coating is removed [1] [5].
to the ones produced at longer test. As can be observed from Figure 8.9 (a), tribological testing of W-S film results in the partial transfer of the material from the coated sample to the counter surface and consequently in formation on the transfer film on the ball wear scar. Further EDS analysis (Figure 8.9 (a)) reveals that the transfer film consists of the coating material and Cr which originates from the interlayer. Hence, it could be deduced that the low-shear-strength tribofilm consisting of layered W-S formed on the ball at the tribological contact area with the W-S film, resulting in lower friction of this material than that of W-S-N films. Due to partially removal of the coating, the measured friction could be actually the friction between the transfer layer and the part of the coating that the ball rests on. Therefore, it is expected that material of W-S film is worn and then adheres on surfaces in the contact forming transfer layer.

On the contrary, micrographs of the ball wear scar obtained during the tribotest of W-S-N films reveals that a stable transfer film is not form and only small islands of adhered material are present (Figure 8.10 (b)-(e)). This could be due to the change in the mechanical resistance and structure when W-S film is doped with N. As mentioned before, W-S coating has crystalline structure, hardness equals to 0.34 GPa and columnar type of structure, while doping this material with a third element often hinders the growth of a crystalline structure and increases hardness. Coating W-S-N2.5 still has crystalline structure, however addition of N significantly increased its hardness and structure compactness what could possible hinder the formation of the stable transfer layer on the ball. Formation of the tribofilm is even more difficult for coatings W-S-N5, W-S-N10 and W-S-N20 due to their amorphous structure.
Figure 8.9: Chemical composition of selected ball scars obtained by EDS after testing at room temperature: (a) W-S, 50k laps, (b) W-S-N10, 50k.

![Chemical Composition Table]

(a)  

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>48.38</td>
</tr>
<tr>
<td>O</td>
<td>33.56</td>
</tr>
<tr>
<td>S</td>
<td>4.97</td>
</tr>
<tr>
<td>Cr</td>
<td>0.62</td>
</tr>
<tr>
<td>W</td>
<td>12.47</td>
</tr>
</tbody>
</table>

(b)  

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>at. %</th>
</tr>
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<tbody>
<tr>
<td>C</td>
<td>55.88</td>
</tr>
<tr>
<td>N</td>
<td>0.00</td>
</tr>
<tr>
<td>O</td>
<td>34.80</td>
</tr>
<tr>
<td>S</td>
<td>0.62</td>
</tr>
<tr>
<td>Cr</td>
<td>4.89</td>
</tr>
<tr>
<td>W</td>
<td>3.81</td>
</tr>
</tbody>
</table>

Figure 8.10: Optical microscope micrographs of ball scars after 50 000 laps of tribological test: (a) W-S, (b) W-S-N2.5, (c) W-S-N, (d) W-S-N10, (e) W-S-N20.

Tribological behaviour at high temperature (200°C)

The average coefficients of friction obtained during the tribological testing of W-S(-N) coatings at 200°C are shown in Figure 8.7. The reported CoF obtained during the 5k laps tests is the average value of the whole test as, in most cases, the 5k laps is the ‘running-in’ period of the test. On the contrary, the reported friction coefficient for
the 50k laps tests is the average 'steady-state’ friction coefficient. The mean coefficient of friction of W-S(-N) coatings is in the range between 0.16 and 0.45, with the lowest value for W-S film and the highest for W-S-N5 film. Coatings W-S-N2.5, W-S-N10 and W-S-N20 have the CoF in the range between 0.35 and 0.41. The CoF measured for the same coating during shorter and longer tests show very similar or equal values. All coatings tested at elevated temperature have the coefficient of friction lower than that of uncoated steel and that obtained at room temperature.

![Graph](image)

**Figure 8.11:** Friction curves for coatings tested for 5 000 and 50 000 laps at 200°C.

The friction coefficient evolution at 200°C is presented in Figure 8.12. The observation of the coatings frictional behaviour reveals that regardless the N content the friction has tendency to stabilize after approximately 5k laps. The only exceptions are coatings W-S-N5 and W-S-N20 which reach a steady-state regime after around 13 000 laps. Obtained steady-state could be possibly related with the formation of the transfer film which could protect coating from wear and consequently results in the stable friction coefficient. Fluctuations in the CoF observed for W-S-N20 film before it reaches the steady-state could be attributed to the gradual formation of a transfer film on the counterpart surface during the early stage of the tribo-test [68]. In order to understand tribological behaviour of tested materials, surface profilometry of the wear tracks, EDS chemical analysis in the wear tracks and on the ball wear scars, as well as microscopic observations were performed.
2D profilometry of the wear tracks was performed in order to measure the wear tracks depth and wear of the coatings. Due to limitations in the measuring equipment it was not possible to obtain the wear profile of most of the coatings. Wear profiles were non-measurable for W-S-N films, hence, it could be deduced that these coatings have good wear resistance and are not worn out throughout the tribological test. The wear track profile was possible to obtain just for W-S film tested for 50k laps. This could be due to significantly lower hardness of W-S film compared to W-S-N films. As reported by

**Figure 8.12:** The mean coefficient of friction of W-S(-N) coatings tested at 200°C: (a) W-S, (b) W-S-N2.5, (c) W-S-N5, (d) W-S-N10, (e) W-S-N20.
Sundberg [1], relatively soft W-S coating is easily sheared what leads to low friction but high wear.

Micrographs of the ball wear scars produced during 50k laps tribological tests at 200°C are presented in Figure 8.14. Micrographs of the the ball wear scars produced during the 5k laps test are not presented as they show the same features compared to the ones produced at longer test. It can be observed that ball wear scars are round and almost completely covered by an adhere and relatively thick transfer film. EDS analysis performed on the ball wear scars after both shorter and longer tribological tests (Figure 8.13) reveals that the transfer layer consists of the coating material. Neither the material of the interlayer or the substrate is detected on the ball wear scar what could suggest that the coatings were not worn out throughout the test. High content of carbon originates supposedly from the environment and the ball material. Nitrogen was not found in the transfer layer and detected in very small amount in the wear tracks. This could indicate that N was released in gaseous form. This assumption agrees with Gustavsson et al. [30] who reported that nitrogen bonded to tungsten can be released due to the reaction of tungsten with oxygen. Comparison of the EDS analysis of the as-deposited coatings (see Table 8.1) and the material in the wear tracks formed after tests at 200°C was made in order to evaluate the difference in the chemical composition. The comparison shows that, in general, there is less S and N, as well as more W, C and O present in the material of the wear tracks. However, more in-depth experiments should be performed to understand the nature of these differences.

From comparison of the ball wear scars after the tribological tests at room temperature and at 200°C it could be deduced that elevated temperature could favour the transfer layer formation. This deduction is based on the properties of TMDs which have proven to work excellent at increased temperature due to the removal of adsorbed water from the surfaces, thus reducing the shear strength and consequently increasing friction [3] [63].
Figure 8.13: Chemical composition of the selected ball wear tracks obtained by EDS after testing at 200°C: (a) W-S, 5k laps, (b) W-S, 50k laps, (c) W-S-N5, 50k laps, (d) W-S-N20, 5k laps, (e) W-S-N20, 50k laps.

Figure 8.14: SEM micrographs of ball scars after 50 000 laps of tribological test at 200°C: (a) W-S, W-S-N2.5, (c) W-S-N5, 50k laps, (d) W-S-N10, (e) W-S-N20.
Chapter 9

Conclusions

The work presented in this thesis is focused on the effect of nitrogen content on the structure, mechanical properties and tribological behaviour of the W-S coating in contact with rubber. The aim has been to gain an understanding of the connection between the composition, structure and mechanical resistance of the coatings, and their tribological behaviour at two temperatures: room temperature and 200°C.

We studied W-S and W-S-N coatings deposited by magnetron sputtering with different partial pressure of nitrogen. The W-S and W-S-N coatings deposited with the lowest N content had crystalline structure, while other W-S-N coatings deposited with higher N content were amorphous. Despite the differences in structure, all W-S-N films exhibited similar mechanical properties and tribological performance. Presence of doping element (N) in the structure led to a significant increase in coatings hardness as well to a change in the coatings morphology. W-S film with columnar cross-section morphology became more compacted due to doping with N. Adhesion of the coatings was considered to be sufficient for tribological testing as at load of 5N, which was used in the tribological tests, coatings were well adhered to the substrate and delaminated zones of the coating from the substrate were not observed.

The results obtained from the EDS analysis, 2D surface profilometry and optical microscopy observation after the tribological tests showed that coatings tested at room temperature for 50 000 sliding cycles were worn reaching high average values of friction coefficient in a range from ~0.6 to 0.73, except of the W-S. W-S film had lower coefficient of friction despite almost complete removal of the coating material. This was due to the formation of a tribofilm in the interface. On the contrary, W-S-N films tested at
200°C were not worn and showed stable coefficient of friction with lower average values coefficients of friction in a range from ~0.16 to 0.45 for test of 50 000 sliding cycles. EDS analysis performed after tests at elevated temperature revealed presence of transfer film on the ball wear scars and did not show either Fe or Cr present in the wear tracks or the ball wear scars. Optical microscopic observations revealed that ball wear scars were covered by transfer film regardless the N content. Formation of a transfer layer corresponded to better tribological properties of tested materials at elevated temperature.

It can be concluded that all tested coatings showed better tribological performance at elevated temperature as compared to room temperature. Hence, it could be deduced that they could be used for applications requiring contact with rubber at temperatures greater than room temperature. However, more experimental testing should be performed in order to confirm this statement.

Coatings tested at 200°C show promising potential. Therefore, this research study will be extended and more experimental testing will be performed. Due to low number of tribological tests performed (one test of 5 000 k sliding cycles and one of 50 000k sliding cycles for each coating), the variance of the results could be high. Repeating experiment for higher number of times could give more statistically improved data. In order to investigate what compounds were formed and how atoms are bonded to each other, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) will be used. Due to the fact that humid air affects frictional properties of TMDs, the tribological tests will be perform in an controlled environmental chamber in dry air conditions. The higher testing temperature will be also used to investigate how it affects he tribological behaviour of tested materials.
Bibliography


Yordanov, M. Investigation of the correlation between internal stresses and adhesion of magnetron deposited CRN coatings for different bias voltage. Indian Journal of Applied Research, 4(11), 2014.


Appendix A

Nanoindentation load-displacement curves

![Image of nanoindentation load-displacement curves for as-deposited films: (a) W-S, (b) W-S-N2.5, (c) W-S-N5, (d) W-S-N10, (e) W-S-N20.]

**Figure A.1:** Nanoindentation load-displacement curves for as-deposited films: (a) W-S, (b) W-S-N2.5, (c) W-S-N5, (d) W-S-N10, (e) W-S-N20.