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DEVELOPMENT AND CHARACTERIZATION OF CrN/CrAlN
MULTILAYER COATINGS DEPOSITED BY HYBRID MAGNETRON
SPUTTERING PROCESS

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DESENVOLVIMENTO E CARACTERIZAÇÃO DE RECOBRIMENTOS
MULTICAMADAS DE CrN/CrAlN DEPOSITADOS POR PROCESSO
HÍBRIDO DE MAGNETRON SPUTTERING

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“Do. Or do not. There is no try.”

Master Yoda

ABSTRACT

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New restrictions and regulations regarding internal combustion engines introduced severe mechanical and thermo-mechanical loads on engine parts, mostly on piston rings, leading to high wear and premature damage, thus causing oil leakage into the combustion chamber and increasing emissions. One of the most viable solutions to overcome these issues is the use of coatings to change surface properties. Coatings produced by High Power Impulse Magnetron Sputtering (HiPIMS) and Direct Current Magnetron Sputtering (dcMS) have shown promising results to form dense coatings with high hardness and high wear resistance. Those properties can be further enhanced by using a periodic structure in the form of multilayers of different materials. In this study, we proposed a hybrid process with HiPIMS and dcMS to produce multilayer coatings of CrN and CrAlN. Different target combinations and negative substrate bias were studied. Furthermore, the base layer influence and an evaluation of the periodicity effects were presented. Structure and morphology of the coatings were characterized with X-Ray Diffraction, Scanning Electron Microscopy and Atomic Force Microscopy. Meanwhile, instrumented nanohardness, corrosion and wear tests were performed to characterize mechanical, electrochemical and tribological properties. Results showed that the choice of target combination and bias values are fundamental for enhancing mechanical and tribological properties. On the other hand, we found no evidence of superlattice hardening when changing periodicity but an increase in corrosion resistance when reducing periodicity was found. The combination of targets, substrate bias, base layer and periodicity presented here showed promising results on wear tests, especially when compared with the current coating under the same engine conditions.

Keywords: sputtering, HiPIMS, hard coatings, multilayer.

RESUMO

CASTILHO, B.C.N.M. **Desenvolvimento e caracterização de recobrimentos multicamada de CrN/CrAlN depositados por processo híbrido de Magnetron Sputtering**. 2018. 106p. Dissertação (Mestrado) – Escola de Engenharia de São Carlos, Universidade de São Paulo, São Carlos, 2018.

Novas restrições e regulamentações de motores de combustão interna introduziram severas cargas mecânicas e termomecânicas no motor, principalmente nos anéis de pistão, o que leva a um alto desgaste e ao dano prematuro dos mesmos e causa vazamentos de óleo na câmara, aumentando as emissões de poluentes. Uma das soluções mais viáveis para solucionar este problema é o uso de recobrimentos para alterar as propriedades da superfície. Recobrimentos produzidos pelas técnicas *High Power Impulse Magnetron Sputtering* (HiPIMS) e *Direct Current Magnetron Sputtering* (dcMS) mostraram resultados promissores na formação de filmes densos com elevada dureza e resistência ao desgaste. Essas propriedades podem ser melhoradas com a utilização de estruturas periódicas na forma de multicamadas. Nesse estudo, foi proposto um processo híbrido de HiPIMS e dcMS para produzir recobrimentos multicamadas de CrN/CrAlN. Diferentes combinações de alvos e de valores de polarização negativa do substrato (*bias*) foram estudadas. Além disso, foram apresentadas a influência da camada base e a avaliação dos efeitos da mudança de periodicidade. Estrutura e morfologia dos recobrimentos foram caracterizadas por Difração de Raios-X, Microscopia Eletrônica de Varredura e Microscopia de Força Atômica. As caracterizações mecânica, eletroquímica e tribológica foram realizadas com ensaios de Nanodureza Instrumentada, Corrosão e Desgaste. Os resultados mostram que a escolha da combinação de alvos e de valores de *bias* são fundamentais para a melhoria das propriedades mecânicas e tribológicas. Por outro lado, não foram encontradas evidências de endurecimento devido ao efeito de super-redes com a variação de periodicidade, mas um aumento da resistência à corrosão foi evidenciado. A combinação de alvos, *bias*, camada base e periodicidade apresentadas aqui mostraram resultados promissores em testes de desgaste, principalmente quando comparadas com os recobrimentos utilizados comercialmente nas mesmas condições de trabalho do motor.

Palavras chave: *sputtering*, HiPIMS, recobrimentos cerâmicos, multicamadas.

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1. INTRODUCTION

Sustainability principles provide the driving force to develop new and cleaner technologies and to improve existing ones. There are worldwide efforts aiming to reduce pollution emissions, mainly enforced and regulated by governments (WONG and TUNG, 2016).

The European Union (EU) was one of the first regions to implement combustion engines emission control. In 1988, the EURO 0, the first attempt to implement such regulations, defined limits for emission of heavy-duty diesel engines and since then regulations are getting stricter. Figure 1 presents the summarized allowed emissions of CO, hydrocarbons (HC), NOx and particulate matter (PM) from 1988 (Euro 0) to 2014 (Euro VI).

According to Figure 1, it is possible to observe a continuous effort to reduce pollutant emission. The NOx emission, for instance, was reduced from 14.4 to 0.4g/kWh and CO from 11.2 to 1.5g/kWh. Over the years, hydrocarbons were reduced by almost 95% and PM was reduced by 97%. All of those are detrimental to the environment, generating problems such as smog, greenhouse effect, acid rain and so forth.

To achieve this emission reduction, engineers and scientists must work in two different fronts: the improvement of combustion process and the quality of the burned fuel. The former is deeply related to the Mechanical Engineering, and thus is an important topic to be discussed and solved.

This issue can be treated by two distinct paths: changing the design, such as the combustion chamber, piston top, etc. thus raising the efficiency of the process. Another way is reducing internal combustion engine losses, by decreasing wear and friction losses. According to Taylor (1993), 15% of the energy generated by the fuel is lost due to friction. Furthermore, 45% of the friction losses are due to the piston assembly, making it the main friction loss.

The wear issue is not limited to engine applications, but it is a broader problem. Recent studies by Holmberg and Erdemir (2017) have shown that 23% of the world energy production is lost due to wear and friction. These two factors are not directly controlled by the restrictions imposed by emission regulations, but the need to reduce emissions changed the combustion process in such way that it imposed higher thermal loads on the engine. This, combined with higher working pressures, led to the failure of engine parts, such as piston and piston rings.

One of the main objectives of piston rings is the sealing of the combustion chamber. As the piston ring is worn out, more oil will be burned in the combustion chamber, thus raising the vehicle emission levels. With the new requirements, old model piston rings could no longer withstand the demands and failed during the operation.

Therefore, it is of utmost importance developing new solutions for piston ring applications, such as using hard coatings on the piston ring surface. This have been widely used to increase tribological performance of materials and have plenty of applications, such as cutting tools, engine parts, medical applications and so forth. There are many processes to produce coatings, each resulting in a different set of properties. Therefore, it is important to know and understand each process to choose the best for the required application.

Currently, piston rings are coated by Cathodic Arc Evaporation, but its performance could not cope with the requirements from Euro VI. Another deposition technique, Magnetron Sputtering, produces harder and almost defect-free coatings, with less residual stresses than its predecessor does, leading to the objective of this study: producing coatings by Magnetron Sputtering hybrid process for piston rings, with higher performance than the ones currently in use.

1.1. OBJECTIVES

This study has as main objective the development and characterization of multilayer coatings of chromium nitride (CrN) and chromium aluminum nitride (CrAlN) with high hardness and high wear resistance.

For that, the following specific objectives are proposed:

- Produce CrN/CrAlN coatings under different conditions of target combination, bias and base layer;
- Characterize the morphology and mechanical properties of the coatings;
- Study the influence of the deposition parameters on the properties;
- Determine the best condition to study the effects of the periodicity variation by optimizing hardness and wear resistance;
- Produce and characterize the coatings with different periodicities to determine the best condition for piston ring application.

2. PISTON RINGS

Since the advent of the first steam engines, pistons have been used to provide movement to the crankshaft. At that time, in the early 18th century, there were huge losses of steam from the chamber and therefore, some sort of sealing was required. Using ropes and hemp was the first attempt to attend this issue and raised the engine efficiency from 0.5 to 5%. It was not until 1854 that the first metal piston ring was produced and, since then, its use and design have been constantly improved (ANDERSSON, TAMMINEN and SANDSTRÖM, 2002).

Nowadays, piston rings are fundamental for the operation of internal combustion engines for the following reasons: they prevent pressure losses during the combustion process; they avoid contamination on the crankcase by combustion products as well as prevent excessive oil from entering the combustion chamber. Furthermore, they are the main responsible to transfer heat from the piston to the cylinder since they are the only part that directly connects the piston to the cylinder liner (BENNETT, 2010; MAHLE, 2010). A schematic of a piston with piston rings is shown in Figure 2.

Figure 2 - Design of a piston ring and its main parts

REF: ANDERSSON, TAMMINEN and SANDSTRÖM (2002).

There are two main classes of piston rings: compression rings and oil control ring. Each class has its own geometry and function (BENNETT, 2010). In Figure 2, it is possible to observe a piston with two compression rings and one oil control ring. Pistons usually have three to five

rings, chosen amongst the two classes, depending on the characteristics of the engine and the requirements of the application (ANDERSSON, TAMMINEN and SANDSTRÖM, 2002).

Compression rings are the first set of rings, closest to the piston top. They are used to seal the combustion chamber and are the main responsible for transferring heat (MAHLE, 2010). They have a diameter larger than the cylinder liner, which contributes to the contact between the surfaces. Furthermore, the presence of the clearances shown in Figure 2 form a path for the combustion gases, which further enhance the contact between the ring and the liner and provide better sealing (ANDERSSON, TAMMINEN and SANDSTRÖM, 2002; MAHLE, 2010; DENTON, 2011). The first compression ring is the one that suffers the highest thermal and mechanical load and therefore it is the one that will be studied in this dissertation. Some of the possible geometry used for compression rings are shown in Figure 3.

Figure 3 - Common designs of compression rings

REF: BENNETT, 2010.

The oil control ring has the main purpose to distribute oil on the cylinder surface and to return the excessive oil to the crankcase by means of the slots present in its structure (ANDERSSON, TAMMINEN and SANDSTRÖM, 2002). Furthermore, it might use a coil spring behind it to provide the required contact pressure between surfaces (MAHLE, 2010). The common examples of oil ring design are presented in Figure 4.

Figure 4 - Common designs of oil control rings

REF: BECO (2018)

The technology behind the production of piston rings is in constant development. Using different materials and hard coatings have been leading the performance increase for this application (MAHLE, 2010). This way, it is possible to combine the mechanical properties of the base ring material with the high tribological performance of the hard coatings (MAHLE, 2010). The ring is usually produced on cast iron or steel, meanwhile there are plenty of options for coatings: chrome plating, nitride-based coatings, thermal spray of molybdenum and diamond-like carbon (DLC) coatings are some of the viable solutions for high wear resistance and low friction (ANDERSSON, TAMMINEN and SANDSTRÖM, 2002; MOBARAK *et al.*, 2014; LIN *et al.*, 2016; WAN *et al.*, 2017).

3. SURFACE ENGINEERING AND DEPOSITION TECHNIQUES

3.1. SURFACE ENGINEERING

Surface engineering is the field of engineering that studies the interaction between surfaces, including the surface modification process and treatments. It has many practical applications: automotive, aerospace, chemical are some of the various industries that can apply the knowledge developed in this area (MARTIN, 2010). Therefore, it is of utmost importance studying and developing new technologies in this area to meet the current demand for high-end applications.

By using surface modification techniques, it is possible to enhance surface properties such as chemical stability, hardness, wear resistance without modifying bulk properties. This provides a unique opportunity to combine bulk and surface properties and optimize them for each application (HOLMBERG and MATTHEWS, 2009; MARTIN, 2010).

Another possibility is combining more than one process. For instance, it is possible to subject the substrate to a thermal or thermochemical treatment, such as cementing or nitriding and then deposit a coating over the surface of the substrate. Therefore, one can create a gradient of properties, further enhancing the product for its applications (HOLLECK, 1990; KELLY and ARNELL, 2000; GE *et al.*, 2013; JIN, DUAN and LI, 2017).

The use of coatings or films to alter surface properties has become a common solution over the last years. There is a wide range of applications in which the use of coatings and films have been applied successfully: optics, electronics and tribological are only but a few of these (KELLY and ARNELL, 2000).

To produce these coatings, one may resort to different deposition techniques, which in turn produce different sets of properties. A few of the deposition techniques available will be discussed over the next section.

3.2. DEPOSITION TECHNIQUES

It is possible to divide the deposition techniques in two major groups. The Physical Vapor Deposition (PVD) and the Chemical Vapor Deposition (CVD). The CVD processes involve the use and reaction of precursor gases to produce coatings and films in a heated substrate. The use of the precursor gases and the need to operate in higher temperatures impose

some limitations to the CVD processes. The resulting gases are often pollutant and dangerous to human health and the high temperature operation might induce phase transformation and defects on the substrate (HOLMBERG and MATTHEWS, 2009).

On the other hand, PVD processes use physical mechanisms to produce the coatings. Within the PVD group, the deposition can occur by either sputtering or evaporation (BUNSHAH, 2001). PVD processes operate in a lower temperature and it is even possible to produce coatings at room temperature (BUNSHAH, 2001). Furthermore, the process gases are usually inert. Therefore, PVD presents a useful solution to overcome the CVD limitations.

Three distinct stages are present in any PVD process. Firstly, there is the formation of the vapor phase. Then, the vaporized atoms must be transferred from the surface of the target to the substrate. Finally, the nucleation and growth of the coating material by the condensation of the vapor on the substrate surface. The control of each of these steps is made independently, which provides coatings with a wide range of properties (BUNSHAH, 2001).

Roughly, the PVD processes are divided in two main classes, regarding the physical method to produce the vapor phase: evaporation or sputtering. A brief overview of the PVD techniques is given in Figure 5.

Ref: Author.

Regarding coating deposition, the Cathodic Arc is one of the main representatives of evaporation process. On the other hand, Magnetron Sputtering is the same of sputtering process. The former is the current method of producing coatings for piston rings and the latter is the proposed alternative in this study to enhance mechanical and tribological properties, which motivates a brief description of both processes.

3.3. CATHODIC ARC

The Cathodic Arc deposition occurs with the formation of an arc due to high current densities on the target surface. This arc allows the evaporation of the target material and the dislocation of the material to the substrate surface. The position in which the arc is formed and the direction of its movement are somewhat unpredictable, which in turn leads to a hard controlling process. The main advantages include a high deposition rate (15 to 20nm/s) and the formation of dense coatings with good adhesion to the substrate. However, the presence of droplets (deposited macro particles formed of pure metal) is a major drawback of this process because it might reduce the hardness and the wear properties of the coating. Although this problem can be overcome by using filters, this solution greatly decreases the deposition rate by 65 to 70%. Another drawback of the cathodic arc process is the lack of control of properties and characteristics of the deposited material (SANDERS AND ANDERS, 2000; HASHMI *et al.*, 2014; ANDERS, 2014).

3.4. MAGNETRON SPUTTERING

The sputtering process consists in using an inert gas to transfer momentum to a target material, removing electrons and ionizing atoms of this material and then moving these to the substrate, thus producing the coating (BUNSHAH, 2001). A basic representation of the process is depicted in Figure 6.

Figure 6 - Schematic of the sputtering process

Ref: HASHMI *et al.*, 2014.

The sputter yield gives a measure of how many atoms are emitted by incident ion and it is an important parameter on sputtering process. It depends on the energy of the arriving ion and of the energy to sputter the target material. This means that it gives an estimation on how hard it is to sputter different materials (WASA, KITABATAKE and ADACHI, 2004; HASHMI *et al.*, 2014). Furthermore, it becomes evident that the choice of inert gas is an important one. Although neon is too small to remove atoms in an effective manner, argon, xenon and krypton make good candidates as inert gases. Due to economical limitations, argon is the most frequent choice for inert gas (MATTOX, 2010).

The use of magnetrons behind the target is a later development and it is used to trap electrons near the target surface, thus enhancing ion formation. The improvement of the ionization process allows for lower working pressures, which increases the mean free path, thus increasing the sputtering rate of the process (BUNSHAH, 2001).

Figure 7 - The trajectory of the electrons on the target

Ref: HASHMI *et al.*, 2014

The sputtering process can be used to deposit a wide range of materials: metals, compounds, ceramics and even polymers. Another possibility is the sputtering of metallic targets in a nitrogen/oxygen/carbon atmosphere, thus forming nitrides, oxides, carbides in a reactive process (OHRING, 2002).

3.4.1. Direct Current Magnetron Sputtering (dcMS)

The simplest method for magnetron sputtering deposition is the Direct Current Magnetron Sputtering, due to the low number of deposition parameters that one needs to optimize during the process. In it, a continuous current is applied to the metallic target and

permanent magnets are used to produce the magnetic field to trap the evaporated species in the region close to the target (HOLMBERG and MATTHEWS, 2009).

Depending on how these magnets are positioned and how strong they are, one might have a balanced or unbalanced configuration (Figure 8). The balanced dcMS confines the plasma to the region close to the target surface reducing the deposition rate and hindering reactive processes. On the other hand, the unbalanced dcMS uses magnets with different intensities, which allow field lines to reach the substrate. This increases not only the deposition rate but also the ion formation, improving coating properties (KELLY and ARNELL, 2000; OHRING, 2002).

Figure 8 - Difference of magnetron configuration on plasma behavior

Ref: BUNSHAH (Adapted, 2001).

3.4.2. High Power Impulse Magnetron Sputtering (HiPIMS)

One of the major limitations of the dcMS process is the power applied to the target. This is caused by the difficulty to keep the cooling of the target. Overheat might permanently damage the target, thus incapacitating it. One possible solution can be achieved by operating with power pulses, which means that more time is given for target cooling. Thus, higher peak power can be achieved without harming target integrity (KOUZNETSOV *et al.*, 1999; SARAKINOS, ALAMI and KONSTANTINIDIS, 2010; ANDERS, 2014).

The High Power Impulse Magnetron Sputtering (HiPIMS) makes use of high peak power and current applied in short pulses, thus increasing plasma density and the ionization of target atoms (SARAKINOS, ALAMI and KONSTANTINIDIS, 2010; HASHMI *et al.*, 2014). A typical curve for a pulse during HiPIMS deposition is shown in Figure 9.

Figure 9 - Typical pulse format for HiPIMS deposition

Ref: HASHMI *et al.*, 2014.

There is plenty of information that can be extracted from Figure 9. The shape of the curve for power and current is usually triangular, but different shapes can be found, depending on the system configuration. The frequency can be defined as:

$$f = \frac{1}{t_{on} + t_{off}} \quad (1)$$

In which:

t_{on} is the time the power source is on

t_{off} is the time the power source is off

Then, the duty cycle can also be defined, which is the time in which the power source is turned on when compared to the whole pulse length:

$$Duty\ Cycle = \frac{t_{on}}{t_{on} + t_{off}} \quad (2)$$

For HiPIMS technique, the duty cycle is usually kept under 10%. This means that a significantly higher peak power can be applied without causing any damage to the target. On the other hand, the deposition rate is significantly lower than the common dcMS and it is usual to find that HiPIMS deposition rate is 20 to 70% of the dcMS deposition rate (ALAMI, BOLZ

and SARAkinOS, 2009). According to Helmersson *et al.* (2006), one possible explanation is the attraction of sputtered ions back to the target region.

Due to the high plasma density, dense coatings with few or no pores are found during HiPIMS depositions. Some other positive effects of HiPIMS are the good adhesion of the coating to the substrate and good surface finish (ALAMI, BOLZ and SARAkinOS, 2007; SARAkinOS, ALAMI and KONSTANTINIDIS, 2010).

The high adhesion to the substrate comes from the fact that it is possible to perform a pretreatment of the substrate before coating deposition. The high energy allows using ion etching, which is a final step of surface cleaning. It uses ionized atoms of the gas or of the target material to hit the substrate surface, thus cleaning it (HELMERSSON *et al.*, 2006; ALAMI, BOLZ and SARAkinOS, 2009; SARAkinOS, ALAMI and KONSTANTINIDIS, 2010). The applied energy is high enough (-300 to -1000V) to avoid the arriving atoms to deposit on the substrate but it provides some degree of ion implantation which also is beneficial to the adhesion (HELMERSSON *et al.*, 2006).

3.4.3. Reactive Sputtering

The deposition of compounds is a viable path to produce hard coatings, such as ceramics. There are two main ways to deposit ceramic coatings. One is utilizing RF-Sputtering to deposit from ceramic targets, a technique that is not discussed in this study, but which has low deposition rate and therefore is not viable for the deposition of thick coatings in industrial scale. Other possibility is to sputter metal targets but introducing reactive gases into the deposition chamber. This process then is called reactive sputtering (HASHMI *et al.*, 2014).

The use of an atmosphere with N₂, O₂ or CH₄ allows the deposition of nitrides, oxides and carbides. Although there is a loss on the deposition rate when compared to the pure metal deposition, the reactive process has higher rate than the RF-Sputtering (BUNSHAH, 2001).

A major drawback of the reactive process is the formation of the compound not only on the substrate but also on the chamber wall and on the target surface. This phenomenon, called target poisoning, have detrimental effects on the sputtering (HASHMI *et al.*, 2014; ANDERS, 2017) and it is one of the main causes of the lower deposition rate of compounds when compared to metals. Furthermore, the process of target poisoning can lead to arcing, which is the concentration of current in one point of target surface, producing an arc, which in turn will produce defects on the coating. Finally, when depositing insulating films, it may happen that

the entire anode region (in this case the anode is the chamber and the substrate) is covered by the film, leading to the disappearing anode problem (HASHMI *et al.*, 2014; ANDERS, 2017).

3.5. INFLUENCE OF DEPOSITION PARAMETERS AND THE STRUCTURAL ZONE MODELS

The deposition of coatings by magnetron sputtering includes the tuning of several parameters. For the most basic process of magnetron sputtering (dcMS), there are at least four different parameters to be adjusted. For an advanced technique such as HiPIMS, this number can be even higher. Thus, a brief description of the parameters influence is introduced and some models describing the relation between process parameters and the morphology are presented.

3.5.1. Pressure

The pressure is one of the main variables to be controlled during the deposition process and it plays a fundamental role for coating deposition. The pressure is related to the quantity of matter inside the deposition chamber by means of the Avogadro's Equation:

$$PV = nRT \quad (3)$$

Furthermore, the pressure is related to the mean free path, which is an average of the distance a particle moves in a space, before hitting another particle. As the pressure is decreased, keeping the other variables constant, the mean free path is increased. This is directly related to the energy of the arriving gas atom at the target and also to the metal atom arriving at the substrate. If an atom leaves the target with a certain amount of energy and hits another particle on its path, the amount of energy of this atom is reduced due to the collision. This will affect the morphology and structure of the coating and it will have detrimental effects on the properties, leading to a more porous coating (OHRING, 2002; MATTOX, 2010; WASA, KANNO and KOTERA, 2012).

Not only the pressure during the deposition is important, but also its control during the beginning of the process is also required. By means of this control, one can remove the impurities (water, gases and vapors) adsorbed at the substrate and target surfaces (MATTOX, 2010).

Several studies describe the influence of the working pressure on coatings properties. Biswas *et al.* (2018a) described the effects of changing the pressure on the formation of defects on HiPIMS multilayer coatings. Lower chamber pressures provided lower defects, which in turn affected different properties, such as corrosion resistance and friction coefficient. Meanwhile, Ganesan *et al.* (2016) have shown that mechanical, optical and electrical properties of an HfO₂ coating can be altered and optimized by varying the chamber pressure.

3.5.2. Temperature

The temperature has the opposite effect of the pressure. If one returns to the physical/thermodynamical meaning of temperature, it is found that it is a measurement of the kinetic/vibrational energy of the particles. Thus, as one increases the deposition temperature, more energetic are the arriving atoms on the substrate. This means that the atoms have more mobility, which in turn reduce the presence of pores, contributing to coating densification.

Studies with different coating materials have shown the dependence of coating properties with the substrate temperature. Among the examples, Gleich *et al.* (2018) showed that not only the morphology of the coating changed (nanograins + amorphous structure to columnar grains) when the temperature varied from 380 to 630°C, but hardness and elastic modulus were significantly increased.

3.5.3. Bias

The negative substrate voltage (bias) by means of an independent power supply is commonly used to increase the energy of the arriving atoms thus giving them more mobility (ANDERS, 2014). This increases coating densification and avoid the formation of voids between columns (ANDERS, 2010). Bias values may vary from 0 to -300V to provide improvement of the properties but higher values increase the residual stress in such manner that it leads to the delamination of the coating (SARAKINOS, ALAMI and KONSTANTINIDIS, 2010).

When the objective is to clean the surface before coating deposition, one might use higher values, from -800 to -1000V. Thus, ion bombardment becomes so energetic that there is no deposition, but only the removal of surface atoms from the substrate, in an ion etching process. Furthermore, those higher values might provide ion implantation on the substrate, below the surface, which increases the adhesion of the coating (ANDERS, 2014).

Biswas *et al.* (2018b) presented in their study a correlation between the applied bias and the quantity of defects on the coatings. Furthermore, they showed that, as the bias was increased, so was the hardness, the corrosion resistance and the surface roughness. Zhang *et al.* (2014) also reported changes in morphology and texture as the bias was increased from 0 to -200V. The H/E and H^3/E^2 was increased for higher values of bias, indicating that wear behavior might be optimized for higher bias.

3.5.4. Frequency and duty cycle

One of the main differences from HiPIMS to dcMS is the presence of an oscillating applied power. For HiPIMS deposition, the usual operation frequency can vary in the range of 10Hz to 10kHz. Both parameters, frequency and duty cycle, can be altered by changing the set t_{on} and t_{off} of the power supply, as defined by Equations (1) and (2). The changes in pulse configuration act in the peak voltage, current and power, thus affecting deposition rate and ion energy (SARAKINOS, ALAMI and KONSTANTINIDIS, 2010).

Hsiao *et al.* (2013) and Chang *et al.* (2014) have shown that by decreasing the duty cycle and keeping a constant frequency, peak power was increased, leading to a more energetic bombardment of ion and increasing the ion density. Although this had great influence on the microstructure, no effects were observed on the hardness of the materials. Another important finding on those studies is that, to increase hardness, bias and/or frequency must be increased, showing a direct relation between these parameters and said property.

Chang *et al.* (2014) also describe how the change on duty cycle from 2% to 100% (dcMS) can influence the deposition rate of a TiN coating. They found that the deposition rate can be increased by a factor of almost three if the duty cycle goes from 2 to 10% and further increased by working with dcMS (100% duty cycle). Furthermore, texture and crystallite size were affected as duty cycle was increased as well as hardness values, which reached a peak at 5% duty cycle.

3.5.5. Power

HiPIMS technique works based on short pulses with high peak power, while it keeps the same mean power than dcMS. Thus, peak power becomes an important variable to be analyzed during coating deposition.

There are several studies showing the effects of changes in peak power on coatings properties. Ferreira *et al.* (2014) presented results that correlate the peak power with deposition rate and grain size. As the peak power is increased, both grain size and the deposition rate are reduced. Höhl *et al.* (1992) showed that increasing of applied power on dcMS system presents the same effect on grain refinement. Furthermore, the residual stresses and hardness were also higher for higher applied powers.

3.5.6. Structural Zone Model

The need to correlate deposition parameters and the resulting morphology of coatings have been a constant subject of study. There are several examples in which these correlations were successfully made, although, because of the many parameters involved in the different deposition process, so far there is no model to describe all the possibilities. The Structural Zone Models (SZM) are the results from these efforts to identify the morphology resulted from the different parameter settings. Even though one might not find the exact SZM for the process, it serves as a guide for the initial parameters settings and to identify the effects of the parameters on the final structure.

According to Bunshah (2001), Movchan and Demchisin made one of the first attempts in this direction, in 1969. They described the relation of the deposition temperature (normalized by the melting temperature of the material) to the morphology in the process of electron beam evaporation (Figure 10).

Figure 10 - SZM proposed by Movchan and Demchisin

Ref: BUNSHAH (2001)

The model shows that three different zones were formed, depending on the temperature used for the deposition and it was developed for different materials (Ti, Ni, W, ZrO₂, Al₂O₃). Zone 1 is characterized by a columnar growth with rounded tops. Furthermore, there are voids and defects between the grains. The growth in this zone is dominated by the low mobility of the arriving atoms. Zone 2 has more uniform columnar grains with the predominance of diffusion of the atoms on the surface. Finally, Zone 3 has recrystallization and bulk diffusion as main formation mechanism, thus leading to wider columns than the previously zones (THORNTON, 1974; BUNSHAH, 2010; SARA KINOS, ALAMI and KONSTANTINIDIS, 2010).

Later, Thornton (1974) developed a more complete model, taking into account the influence of the gas pressure in his model (Figure 11) for a magnetron sputtering process.

In addition to the new axis for pressure, Thornton model also include a new zone, called Zone T, which is a transition between Zones 1 and 2. It is characterized by a dense structure, without the presence of voids between the grains.

Figure 11 - Thornton model for a magnetron sputtering process

Ref: HOLMBERG and MATTHEWS, 2009.

Anders (2010) published a model for HiPIMS coatings (Figure 12). It used the same division of four zones (Zone 1, T, 2, and 3), but included an axis representing coating thickness (z-axis). Furthermore, the temperature axis is not only described by the homologous temperature but it takes into consideration the effects of the potential energy, which causes

changes in the temperature. The axis with pressure information was changed by one with information regarding the kinetic energy of the arriving ions (ANDERS, 2010).

Figure 12 - Anders model for HiPIMS deposition

Ref: ANDERS, 2010.

One of the main features of the model proposed by Anders is the effect of the kinetic energy on the thickness. It is possible to observe that, as the energy is increased (which can be altered by changing the substrate bias) the coating thickness decreases, up to a point where no coating is deposited and the only effect is the ion etching of the substrate. Anders also describes a change in the residual stresses from tensile to compressive, which occurs in the Zone T (ANDERS, 2010).

The models presented here are just a brief representation of the deposition process and do not provide a full perspective of all the effects of the deposition parameters. There are continuous efforts to characterize the influence of the parameters on the properties and morphology of the coatings. Thus, this is a field of study in constant development.

4. MATERIALS

This study will focus on the development of CrN/CrAlN multilayer coatings. Thus, a brief review of CrN and CrAlN coatings is done, as a mean to describe some basic properties and what is expected to achieve. Furthermore, the effects of the presence of multilayers and superlattice structures is discussed.

4.1. CHROMIUM NITRIDE (CrN) COATINGS

Metallic nitrides have been widely used to produce coatings with high chemical stability and good mechanical and tribological properties. Chromium nitride coatings have been used to replace titanium nitride because the former have higher chemical stability at higher temperatures applications (STEYER *et al.*, 2003). Furthermore, CrN coatings present high hardness and high wear resistance (HOLMBERG and MATTHEWS, 2009; LIN *et al.*, 2010; GUIMARAES *et al.*, 2018).

It is well known that coating properties are deeply related with deposition process and parameters. Low quantities of nitrogen, for instance, leads to the formation of Cr₂N, which has different properties than CrN (AOUADI *et al.*, 2001; LIN *et al.*, 2011). Properties such as corrosion resistance is related to the presence of pores, which in turn is related to deposition process. Some studies have shown that CrN deposited by three different methods (Cathodic Arc, Magnetron Sputtering and Electron Beam Evaporation) presented different outcomes for hardness and roughness. All coatings showed high wear resistance, and the Cathodic Arc coating had the highest of them all, even though it had highest roughness (FUENTES *et al.*, 2005).

Furthermore, studies have shown that chromium nitride coatings have been used in a diversity of applications. Recently, Arif, Sanger and Singh (2018) showed that CrN deposited by dcMS can be used as electrodes for supercapacitor.

Chromium nitride has a faced centered cubic structure of the NaCl type. Nitrogen occupies the octahedral interstices of the lattice. Furthermore, the bulk CrN has a density of 5.9g/cm³ (but coating density might vary with deposition process and parameters) and the melting temperature of 1770°C.

4.2. CHROMIUM ALUMINUM NITRIDE (CrAlN) COATINGS

Another useful option for reducing wear and increasing hardness is adding of aluminum on metallic nitrides.

Studies have shown that the addition of aluminum up to 68%at. on coating composition provides increasing hardness values. This addition also contributes to increase corrosion and oxidation resistance even when compared with CrN, TiN and TiAlN (BRIZUELA *et al.*, 2005; BOBZIN *et al.*, 2007; DING *et al.* 2008; CHIM *et al.*, 2009). There is no change on the CrN face centered cubic (FCC) structure up to 60%at aluminum addition, since the element acts as substitutional element on the lattice, reducing the lattice parameter (KIMURA *et al.*, 2003).

From 60 to 68%at, the crystalline structure changes from FCC to hexagonal but hardness continues to grow due to the formation of small hexagonal precipitates. With further aluminum addition, these precipitates grow and the material loses the desired mechanical and tribological properties (KIMURA *et al.*, 2003). Kimura *et al.* (2003) also presented results describing how the lattice parameter of CrAlN changed (shrunk by 1.22%) by with increasing Al content up to 60%. After 70%, the crystalline structure changes to a hexagonal one.

4.3. MULTILAYER AND SUPERLATTICE STRUCTURES

Multilayers can be produced by different means, either for PVD and CVD depositions. For CVD, it is enough to change the precursor gases or process temperature, thus forming different layers of coating. Magnetron Sputtering operates on a line-of-sight base, meaning that the sample must be in front of the target to the deposition occur on the surface. This issue is addressed by rotating the sample in front of multiple targets with different compositions. Another possible path is changing gas composition, thus enabling different compounds or a gradient to be formed. In this study, when multilayers are mentioned, the reader must bear in mind that the former process has taken place to produce the coatings.

Figure 13 illustrates the difference between multilayers and superlattice. In a general manner, when each individual layer has thickness of 5 to 25 nanometers, it might be called superlattice (CAVALEIRO and DE HOSSON, 2006; HOLMBERG and MATTHEWS, 2009). The thickness of two or more consecutive layers is defined as periodicity (Λ).

Figure 13 - Schematic difference between multilayer and superlattice

REF: HOLMBERG and MATTHEWS (2009)

Although the use of multilayer is not directly related to an increase in hardness, there is always an increase in the resistance to crack propagation associated to its production. This is mainly related to the deviation of the fracture at the interface between layers (STUEBER *et al.*, 2009). On the other hand, superlattices present, besides the said increase in fracture propagation resistance, a lower residual stress than single component coatings and, in general, an increase in hardness as the periodicity is reduced. Some studies show that, for periodicities lower than 5nm, the effect of enhanced hardness is no longer present (Figure 14) (CAVALEIRO and DE HOSSON, 2006; HOLMBERG and MATTHEWS, 2009).

Figure 14 - Relationship between hardness and periodicity of different material combinations

Ref: CAVALEIRO and DE HOSSON (2006).

Figure 14 shows the hardness results for different combinations of materials in multilayer structures with different periodicities. It is possible to observe that, for Ti-based coatings, a strong increase in hardness is found when the periodicity is reduced up to 5nm. Then, for lesser values, hardness drops abruptly for these coatings. Kim, Byun and Han (2009).

deposited CrN/CrAlN coatings with different periodicities (ranging from 4 to 44nm) to evaluate its influence on coatings properties. Similar trending as the one presented, in which a maximum value was reached for 5.5nm (46GPa) with significant decrease for values lower than this.

Araujo *et al.* (2015) reported an increase of hardness up to 3200HV for 4nm periodicity, in a multilayer coating of CrN/NbN produced by cathodic arc evaporation. Furthermore, an increase in the critical load to failure at the scratch test was observed for coatings with reduced periodicity.

The mechanism behind the superlattice hardening can be explained by the fact that the periodicity is so small that the mechanisms responsible for generating dislocations cannot actuate properly. Furthermore, the presence of interfaces between the layers hinder the movement of the dislocations, which are the main cause of plastic deformation in materials (KOEHLER, 1970; HULTMAN, ENGSTRÖM and ODÉN, 2000). By making the production and movement of dislocations difficult, it is possible to increase the hardness of the material (ABBASCHIAN, ABBASCHIAN and REED-HILL, 2009).

For a compatible superlattice structure, some requirements have to be met: the coefficient of thermal expansion and the lattice parameter of the components should not be too discrepant and the bonding energy between different atoms should be approximately the bonding energy between similar atoms and the elastic constants of the two materials should be as different as possible (KOEHLER, 1970).

5. METHODOLOGY

In this section, it will be described the experimental procedure for the coating deposition and the techniques used to characterize the coatings.

5.1. EXPERIMENTAL SETUP

Coating deposition was made at the PVD pilot plant located at EESC-USP. The high vacuum chamber Plasma-HiPIMS-250 was built by PLASMA LIITS. It has four target positions and a planetary carousel to provide an evenly deposition on piston rings. The chamber has two heating resistances to heat the samples; each resistance has one thermocouple for temperature monitoring. Furthermore, another thermocouple is installed at the chamber center, which works as an estimate for the temperature of the samples. Figure 15 shows the chamber closed (a) and opened (b).

Figure 15 - Deposition chamber: (a)closed, (b) opened

Ref: Author.

The outer structure and the targets are refrigerated by two closed systems of water cooling operating at 18°C all the time (blue hoses). In Figure 15 (b), it is also possible to observe the piston rings positioned on the carousel and ready to start the deposition process.

For this study, only three of the four targets were operational and the combination of uses of Cr or CrAl targets is one of the subjects that will be addressed in this study. All coatings used targets of Cr and CrAl (50-50%at) with 99.5% purity and dimensions of 214x106x12mm. In Figure 16, one of the targets is shown in two different states of use.

Figure 16 - CrAl targets: (a) new target; (b) target after a series of depositions

Ref: Author.

It is worth noticing the wear of the target after some depositions. The racetrack, the region where electrons travel, is clearly seen in Figure 16 (b). For coating deposition, three MDX Pinnacle (Advanced Energy, USA) power supply were used (two DC and one as bias). Furthermore, one Truplasma HighPulse 4004 (TRUMP Hüttinger, Germany) was used as HiPIMS power supply.

Figure 17 shows a schematic of the top view deposition chamber.

Figure 17 - Top-view schematics of the deposition chamber

Ref: The author.

By analyzing Figure 17, it is possible to observe the position of the supports, magnetrons, heaters and samples. The carousel rotates around the Z-axis, meanwhile the ring and the samples rotate with the support. Thus, the support rotates in its own center meanwhile moves with the carousel. The sequential exposition of the substrates (both ring and flat sample) to the different targets produces the desired multilayer effect. Furthermore, as the speed of the carousel and consequently of the support is changed, the thickness of each deposited layer is changed, which allows the variation of the periodicity.

5.2. COATING DEPOSITION

The coating deposition process starts with the sample preparation. In this project, each batch consisted of 10 rings and 1 flat sample.

5.2.1. Sample preparation

Two different sample preparation method had to be used in this study, due to the different nature, format and material of the rings when compared to the flat sample.

5.2.1.1. Rings

The AISI 440 stainless steel rings had 131mm outer diameter, 126mm inner diameter and 3.5mm thickness as depicted in Figure 18. They were previously nitrided with a resulting layer of approximately 60 μ m. Before inserting them in the chamber, they were cleaned with acetone and ether to remove any residual impurity such as grease and oil.

Figure 18 - Heavy-duty piston ring used for coating deposition

Ref: Author.

5.2.1.2. Flat Sample

A 30mm diameter cylindrical flat sample of AISI 304 austenitic stainless steel was inserted in the chamber with the rings. These samples were grinded on 120,240, 600, 1500, 2500 sand paper and then polished with diamond paste of 15, 6, 3 and 1 μ m. To provide a mirror finish surface, the samples were polished with colloidal alumina 0.05 μ m. Then they were ultrasonically cleansed in an acetone bath.

5.2.2. General Deposition Parameters

The first step of the coating deposition is the ion etching, during which Cr^+ ions produced by sputtering in an argon atmosphere are used to provide a final cleaning of sample surface and to create a thin layer of Cr implantation. The samples were subjected to the ion etching for one hour. The parameters used in this stage can be observed in Table 1.

Table 1 - Ion etching parameters

<i>Parameter</i>	<i>Value</i>
<i>Target</i>	Cr – HiPIMS
<i>Power [W]</i>	600
<i>Voltage [V]</i>	1000
<i>Gas</i>	Ar
<i>Gas flow [sccm]</i>	40
<i>Bias [V]</i>	-800
<i>Frequency [Hz]</i>	104
<i>Pulse length [μs]</i>	50

Ref.:Author.

Then, the second step is the deposition of the base layer. In this project, some different possibilities were explored for the base layer composition, which will be informed over the next sections.

The last stage is the coating deposition. Some parameters were kept the same for all depositions; those are informed in Table 2.

Table 2 - Fixed parameters for coating deposition

<i>Parameter</i>	<i>Value</i>
<i>N_2 flow rate [sccm]</i>	50
<i>Ar flow rate [sccm]</i>	40
<i>Power [W]</i>	900
<i>Frequency [Hz]</i>	500
<i>T_{on} [μs]</i>	200
<i>Duty Cycle [%]</i>	10
<i>Deposition time [hours]</i>	20

Ref. Author.

5.2.3. Experimental planning

This study was divided in four optimization stages, which can be observed in Figure 19.

Figure 19 – Flow chart exhibiting all the stages of coating development in this study

Ref: Author.

Initially, this study would consist of two stages: a first stage aiming to decide which of the possible target combinations would provide higher hardness. Then, a second stage to evaluate the effects of the periodicity on the mechanical properties of the coating. However, during the development of the study, more stages were required for further enhancing the desired properties. All these stages and the explanations on why they were required will be subsequently described on the next chapters.

After defined the best deposition parameters, the periodicity of the multilayer coating and its influence on mechanical and tribological properties were evaluated. All parameters were kept constant and only the velocity of the support (carousel) was varied. As the velocity is increased the periodicity is expected to be reduced because the sample will spend less time facing the target in each rotation. Thus, four different speeds were proposed: 0.5, 1.0, 1.5 and 2.0rpm.

5.3. COATING CHARACTERIZATION

The produced coatings were characterized by its morphology, structure and mechanical and tribological behavior. The morphology was evaluated by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The structure and phase composition was evaluated by X-Ray Diffraction (XRD) and the mechanical characterization used Nanohardness and Wear tests. Furthermore, the corrosion behavior of the coatings were also evaluated. All these techniques will be briefly described in this section.

5.3.1. Scanning Electron Microscopy

The Scanning Electron Microscopy (SEM) is a technique that uses an electron beam to interact with matter. During this interaction, different signals are generated which can be collected and analyzed, thus producing a variety of information (GOLDSTEIN *et al.*, 2003; REIMER and KOHL, 2008). A representation of the physical effects occurring during the electron-matter interaction can be observed in Figure 20.

Figure 20 - Interaction between electron beam and sample generating signals

Ref: CCWJ, 2018.

There are several analysis that can be performed by collecting the emissions showed in Figure 20. Secondary Electrons (SE) are the ones emitted closest to the surface and therefore they provide information regarding the studied material topology. On the other hand, Backscattered Electrons (BSE) give chemical contrast because of a more pronounced backscatter of electrons by heavier elements. This provides a qualitative comparison of chemical composition as lighter materials appear darker on the image and heavier materials appear brighter (GOODHEW, HUMPHREYS and BEANLAND, 2001; OHRING, 2002; GOLDSTEIN *et al.* 2003).

Finally, it is possible to quantify chemical composition by using the X-Ray emitted from the interaction. By using Energy-Dispersive X-Ray Spectroscopy (EDX) the X-ray data is collected and the spectrum is compared to standard energy values for the elements (GOLDSTEIN *et al.* 2003)..

In this study, a FEG-SEM Inspect F-50 (FEI, The Netherlands) was used to characterize the morphology of the coatings. The energy of the beam was set at 5kV for cross-

sectional/fracture images and 10kV for top images. For all images the spot was 3.0 and the working distance approximately 10mm.

5.3.2. Atomic Force Microscopy

The Atomic Force Microscopy is a versatile technique to characterize materials. It has high height resolution (Z-axis resolution) in the order of angstroms and under special conditions can be used to image atoms. The basic setup is depicted in Figure 21. It consists in a tip connected to a cantilever, which in turn is connected to the controller. Meanwhile a laser is reflected by the backside of the cantilever. Thus, when the tip reacts to an applied force or an obstacle, the reflection changes its position. A feedback is given to the controller which adjust the position of the cantilever. The AFM cantilever might operate in a constant deflection or constant force mode. On the former, the force is adjusted to keep the same deflection of the cantilever. The latter keeps a constant force by changing the position of the cantilever (YAO and WANG, 2005; REIFENBERGER, 2016).

Figure 21 - Schematics of the AFM PID controller

Ref: YAO and WANG (2005).

Regarding the nature of the interaction force, or operation modes, AFM has three major configurations: Contact, Non-Contact and Intermittent (or Tapping), which can be observed in Figure 22. On the first, the AFM tip is in permanent contact with the surface, hence increasing the wear of the tip and with higher risks of tip contamination. In the Non-Contact mode, the tip never touches the surface but it operates on forces generated between the bonds of atoms of the tip and the surface (Van der Waals forces). Finally, in the Tapping mode the tip hits the surface

at given frequency. This reduces the wear of the tip and decreases the chances of sample damage when compared to the Contact mode (REIFENBERGER, 2016).

Ref: BALTHAZAR *et al.* (2012).

The AFM can measure roughness by using the principle described above, but it is not limited to that. By measuring the electrical interaction between the sample and a metal-coated tip, it is possible to characterize the electric response of the material in different regions of the surface. The magnetic forces can also be measured, hence showing the magnetic domains of a material. For those, the Non-Contact mode is ideal, to prevent electric contact between surface and tip. On Contact mode, it is possible to measure different elastic responses of the material, which has great application on the study of polymers (YAO and WANG, 2005).

For this study, we operated the Atomic Force Microscope on Tapping Mode. The images were made on an area of $30 \times 30 \mu\text{m}$, with 512 lines and 2 seconds per line. PID configuration was adjusted as required by each sample morphology as a mean to prevent the formation of artifacts. The software Gwyddion was later used to process the data, calculate roughness values and to build the 3D images.

5.3.3. X-Ray Diffraction

The X-Ray Diffraction technique is mostly used to study the crystallographic structure of materials. With it, it is possible to determine a diversity of information from samples, such as phase distribution, residual stresses, texture, microstrain and crystallite size. Therefore, the fundamentals of the technique and some advanced analysis will be discussed in this section.

5.3.3.1. Fundamentals

X-rays are used in a wide range of applications. Since the space between atoms in a crystalline structure is approximately of the same order of the wavelength of the X-Ray, both constructive and destructive interference is produced. Bragg's law sets the constraint for which constructive interference happens for a given combination of wavelength, interplanar spacing and incidence angle (Figure 23) (CALLISTER, 2007; WASEDA, MATSUBARA and SHINODA, 2011).

Figure 23 - X-Ray Diffraction working principle

Ref: CALLISTER, 2007.

Thus, Bragg's law is given by:

$$n * \lambda = 2 * d_{hkl} * \sin \theta \quad (4)$$

Furthermore, for cubic lattice structure, the interplanar spacing is given by:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (5)$$

In which a is the lattice parameter and h, k, l are the Miller indices.

The θ - 2θ geometry is the most used regarding crystallographic analysis. There are two main ways to perform a θ - 2θ scan: either the source of the x-ray is fixed and then the sample

rotates in a θ angle and the detector in a 2θ angle or both source and detector can move in a θ angle (BIRKHOLZ, 2006).

For this study, we used a Rotaflex Ru200B (Rigaku, Japan) with a copper rotatory anode tube ($K\alpha$ - 1.5418Å) in a θ - 2θ geometry. The scan was made with 2θ changing from 35° to 85° , beam acceleration of 40kV, beam current of 60mA, steps of 0.05° , acquisition time of 5s. Data analysis was made using the X'Pert High Score Plus.

5.3.3.2. Texture

For a polycrystalline sample, one may assume that all orientations will occur with the same probability. However, depending on factor such as production method or how the sample was processed (laminated, welded, etc.), grain orientation might change as a result, thus one will find the grains arranged in a preferential orientation. This phenomenon is called texture, or preferential orientation. For thin films, this is an important topic since it can influence optic, electric, mechanical and wear properties. (GOTTSTEIN, 2004; BIRKHOLZ, 2006; ABBASCHIAN, ABBASCHIAN and REED-HILL, 2009)

The texture can be observed in a θ - 2θ scan as an increase of the intensity in one or more peaks if compared to the powder diffraction of the same material. Thus, one method to determine the preferred orientation is the texture coefficient, which compares each intensity of the measured sample to a reference powder diffraction. Because it is a simple method, the texture coefficient is one of the most used to estimate texture and can be calculated by Equation 06 (BIRKHOLZ, 2006):

$$T_h = \frac{I_h^m / A_{\theta 2\theta}(\theta_h)}{I_h^{ICDD}} \cdot \frac{\sum_h I_h^{ICDD}}{\sum_h I_h^m / A_{\theta 2\theta}(\theta_h)} \quad (6)$$

In which:

I = Intensity

Index m = measured

Index ICDD = powder reference

$A_{\theta 2\theta}(\theta_h)$ = absorption factor, given by:

$$A_{\theta 2\theta}(\theta_h) = 1 - e^{-\frac{2\mu t}{\sin \theta}} \quad (7)$$

In which:

μ = linear attenuation coefficient (1215cm⁻¹ for Cu radiation on CrN coating)

t = coating thickness

For texture calculations, the data acquired by the Rigaku diffractometer on the θ -2 θ scan was used and analyzed, with the help of the software PeakFit.

5.3.3.3. Satellite peaks

When dealing with superlattice coatings and structures, the XRD data will not only provide information about the lattice structure but also about the coating periodicity. This happens because not only the lattice parameter is on the same magnitude of the X-ray wavelength, but also the space between each layer is in the same magnitude. Thus, for lower periodicities, one might find the satellite peaks which appear around a central peak as shown in Figure 24 (WASA, KITABATAKE and ADACHI, 2004).

Figure 24 - Example of satellite peaks in a superlattice CrN/NbN XRD

Then, one might calculate the periodicity by using equation 8, which relates the sine of the theta angle measured for each satellite peak to the periodicity:

$$\Lambda = \frac{|m - n|\lambda}{2|\sin(sa_m) - \sin(sa_n)|} \quad (8)$$

In which:

Λ is the periodicity;

m, n are the peak order

λ is the x-ray wavelength

5.3.4. Nanohardness

The hardness test is one of the most used tests to provide information of mechanical properties of materials because of its simplicity and fast results provision. In general, it uses a tip to apply a determined load to the material surface, thus making an impression. This is related to the resistance to plastic deformation (MARTIN, 2010; FISCHER-CRIPPS, 2011). Then, hardness values are obtained by measuring this impression and the applied load. However, when it comes to thin films, standard hardness tests no longer can be performed, since the applied loads are too high.

When a high load is applied on a thin film, one will measure not only the hardness of the coating but also of the substrate (BUNSHAH, 2001). As the substrate usually have lower hardness than the coating, this is not desirable. To guarantee that no influence of the substrate is found on the measurements, it is required that the penetration depth is less than one tenth of the total coating thickness (BUNSHAH, 2001). However, standard hardness tests cannot provide such control nor loads small enough to avoid this (BUNSHAH, 2001)..

The use of the instrumented nanohardness test allows lower loads to be applied and gives instantaneous depth information during the measurements (OHRING, 2002). Furthermore, by the curve produced during the measurement, it is possible to determine the elastic module of the coating (OLIVER and PHARR, 1992). Thus, since its development, the instrumented nanohardness test has become a common choice for the evaluation of hardness and elastic modulus of thin films.

Different test methods uses different combinations of loads and indenters to make the impression (Brinell – spherical; Vickers – pyramidal; Rockwell – spherical or conical). For nanohardness test, one of the most common indenter is the Berkovich, which is a three-sided diamond-made pyramid (Figure 25).

Figure 25 - SEM image of a Berkovich indenter

Ref: NAP-MA USP, 2016.

A standard load-unload curve resulted of a nanoindentation test with a Berkovich indenter is shown in Figure 26.

Figure 26 - Typical load-unload curve during nanoindentation test

Ref: OLIVER and PHARR (2004).

During the test, the displacement h and the load P are continuously measured. From the curve, four values are extracted: the maximum load and depth ($P_{\max}$ and $h_{\max}$, respectively), the elastic unload stiffness (S) and the final depth (h_f). Then, hardness (H) is given by:

$$H = \frac{P_{max}}{A} \quad (9)$$

In which:

$$A = F(h_c) \quad (10)$$

is the area function. Meanwhile:

$$h_c = h_{max} - \epsilon \frac{P_{max}}{S} \quad (11)$$

To clarify the physical meaning of h_c , Figure 27 is presented:

Figure 27 - Cross-section view of an indentation

Ref: OLIVER and PHARR (2004).

Figure 27 shows a cross-sectional view of the hardness test in three different stages: before indentation, during the indentation at maximum load and after the load is removed. Thus, it is possible to observe that h_f is the final depth after the load is removed. Furthermore:

$$h_{max} = h_s + h_c \quad (12)$$

Then, h_s is the amount of sink in, when the pile-up is negligible. Since it is in the elastic regime, it is given by:

$$h_s = \epsilon \frac{P_{max}}{S} \quad (13)$$

In which ϵ is related to the geometry of the indenter (Berkovich = 0.75). By the substitution of equation 11 on equation 12, one arrives at equation 13.

On the other hand, the calculation of the elastic modulus is given by:

$$S = \beta \frac{2}{\sqrt{\pi}} E_{eff} \sqrt{A} \quad (14)$$

And:

$$\frac{1}{E_{eff}} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i} \quad (15)$$

In which ν is the Poisson ratio and E is the elastic modulus. Furthermore, the index i refers to the indenter. During the development of the nanohardness test, β was considered equal to 1. Further studies with numerical simulation proved that, depending on the geometry of the indenter, this constant might change from the unity. For the Berkovich indenter, values were found on the literature from 1.0226 to 1.085 (OLIVER and PHARR, 2004).

In this study, a PB1000 Mechanical Tester (Nanovee, USA) was used to perform the measurements. Fifteen measurements (3x5 matrix) spaced with 50 μ m apart. The maximum load was 30mN with load/unload rate of 60mN/min. After the measurements, each curve was analyzed to determine the starting point of contact and the mean hardness and elastic modulus and the respective deviations were calculated.

5.3.5. Wear test

The wear test provides meaningful information regarding the behavior of different materials when these are in contact. Thus, it is a very specific test and wear properties are deeply related to the tribological pair in study as well as the conditions of the test (lubrication, temperature, humidity, and so on).

Different mechanisms (adhesive, abrasive, chemical or fatigue) and modes (sliding, rolling, fretting, erosion, etc.) of wear can be found during these tests and sometimes a combination of mechanisms and modes can be found. Thus, it is necessary to find a test that describes as close to the real application as possible (MENEZES *et al.*, 2013).

There are many ways in which the wear test can be performed. Pin on disk, pin on flat and the calowear are some of the possible configurations to study the wear resistance behavior of materials (Figure 28). As the tribological pair play a fundamental role on wear behavior, we decided to perform this test under similar conditions of the engine. This means that we opted to use the ring in contact to the cylinder liner. This way, we could evaluate wear performance taking in consideration the roughness of the ring, the materials used, similar lubrication and forces acting inside an engine.

Figure 28 - Common wear tests: (a) pin on flat; (b) pin on disk; (c) calowear

Ref: A- MECHACTION, INC (2018); B- HWANG, LEE and KIM (2015); C- RANDAL (2013).

In this study, coated segments of piston rings were tested against a gray cast iron counterpart (cylinder liner). The load was set in 360N and a speed of 900rpm (idle engine) was used. The tests were performed for two hours under lubrication with an oil 0W20 and Al_2O_3 abrasive (5g/L) at a temperature of 130°C. Four segments of each ring was made and tested, then the results were averaged.

5.3.6. Corrosion

Figure 29 presents a common method for determining the current and potential of corrosion, called Tafel Extrapolation method. It consists on tracing two tangents to the anodic and cathodic curves and the values of the corrosion potential and current is given by the x and y coordinates of the intersection of these tangents (POPOV, 2015).

Figure 29 - Tafel Extrapolation Method

Ref: POPOV (2015).

The corrosion experiments were performed in a Potentiostat Galvanostat PerkinElmer VersaSTAT4, with an exposed area of 0.76cm^2 . A NaCl solution (3.5%) was used and the potential was analyzed from -0.25V to 0.25V with scan rate of 0.167mV/s .

6. RESULTS AND DISCUSSION

This section will describe and discuss all the achieved results. Furthermore, a detailed description of each step taken in this study will be given to justify the chosen path during the research. It will be divided in four parts, one for each stage described on the methodology.

6.1. FIRST STAGE – TARGET COMBINATION

The first stage of this study consisted in the exploration of the possibilities of using different target materials under different power sources to find the best possible combination. The main aim was to maximize hardness and wear resistance.

Thus, three different combinations were proposed, as shown in Table 3.

Table 3 - Deposition parameters for the first set of depositions

Sample name	M01	M02	M03
Bias [V]	-120	-120	-120
Carousel Speed [rpm]	1.0	1.0	1.0
Base Layer	Cr+CrAl	None	Cr
Base Layer Deposition Time [hrs]	2		
Target (Base layer)	Cr HiPIMS + Cr DC+ CrAl DC	None	Cr HiPIMS
Atmosphere (Base layer)	Ar (40sccm)		
Target (Coating)	Cr HiPIMS +Cr DC + CrAl DC	Cr HiPIMS + 2 CrAl DC	CrAl HiPIMS + CrAl DC + Cr DC

Ref.: Author.

After the deposition, the first precaution for coating characterization was to determine the deposition homogeneity and uniformity on the ring and throughout the different rings on the column. Therefore, SEM images were made of the cross-section of the rings in three positions of the same ring and in different rings of the column, all of the M01 coating. The ring was arbitrarily divided in three positions separated 90° from each other: 0°, 90° and 180°. For evaluation in different positions of the column, a ring from top, bottom and middle were cut

and evaluated. The results are shown in Figure 30 (a) and (b), respectively, and Table 4 compiles the measured results.

Figure 30 - Evaluation of coating thickness and morphology of rings from the same batch in different position by SEM images

Ref: Author

Table 4 - Results of the thickness measurement for the first experiment

<i>Position</i>	0°	90°	180°	Ring 1	Ring 5	Ring 10
<i>Thickness [µm]</i>	13.3 ± 0.3	12.6 ± 0.2	12.8 ± 0.2	12.6 ± 0.2	13.0 ± 0.3	13.0 ± 0.1

Ref.: Author.

Results show small variation of coating thickness for all the different positions tested. This indicates good reproducibility and therefore corroborate the decision to perform the analysis by image of just one ring per batch.

The base layer of the M01 concept was produced with a multilayer structure of Cr+CrAl. Since the deposition rate of the metals is higher than the ones from nitrides, it was possible to evaluate the periodicity of the base layer and validate a method for estimating periodicity using SEM images, which can be observed in Figure 31.

Figure 31 - SEM image showing multilayer (Cr+CrAl) on the base layer

Ref: Author

To estimate the periodicity, one must assume the deposition rate constant throughout the time. The bilayer periodicity can be considered as the thickness deposited in one complete rotation. The coating thickness is then the total thickness deposited after all the rotations, or in other words, the coating thickness is the sum of all the deposited bilayers. Therefore, based on the measured thickness, on the deposition time and on the rotation speed it is possible to estimate the periodicity by:

$$\Lambda [\mu m] = \text{thickness} [\mu m] / (\text{time} [\text{hours}] * \text{speed} [\text{rpm}] * 60) \quad (16)$$

The base layer periodicity was measured by Figure 31 and a result of 20.7nm was found. Using the formula on Eq. 16 the calculated periodicity was 20.8nm. Therefore, the equation proposed to estimate the periodicity showed good agreement with the true measured value and it will be used to estimate the periodicity of all coatings.

SEM images of the concepts M02 and M03 were also analyzed and the total thickness measured by Figure 32.

Figure 32 - SEM images of the three different coating concepts

Ref: Author.

Based on the analysis of Figure 32, no significant difference in microstructure is observed. The three samples present effects of the shadowing, in which columnar grains start small and grow in a cone-like structure. This had been reported in literature as a sign of low energy during the deposition (Thornton, 1974; Anders, 2010). It is also possible to observe the absence of base layer on coating M02, and the thicker base layer of M01 when compared to M03, due to the use of three targets to deposit the former instead of one of the latter.

Measurements of thickness were made based on the SEM images shown in Figure 32 and are presented in Table 5. As the deposition rate of the CrAlN is lower than the CrN, higher deposition rate of the M01 sample is justified, as this was the one with higher number of Cr targets.

Table 5 - Total thickness and deposition rate for the first set of samples

		M01	M02	M03
Thickness [μm]	Total	14.9±0.2	11.4±0.3	11.3±0.1
Deposition Rate [μm/hr]	Base layer	1.2	-	0.35
	Coating	0.625	0.57	0.53

Ref.: Author.

The top morphology was also characterized for these experiments, with two distinct magnifications (Figure 33 and Figure 34), to characterize the different features of the coatings.

Figure 33 - SEM top view of the three different concepts

Ref: Author.

From Figure 33, it is possible to observe that the coating covered the entire region but followed the surface features that were present on the ring before the deposition process. This means that the ring initial surface roughness can be observed as the horizontal stripes of the coating. In general, Magnetron Sputtering deposition techniques have been reported to have good surface cover, which means that this was an expected result from the deposition. Furthermore, this means that the substrate surface finish is an important variable for this process.

Figure 34 - Detailed view of coatings top morphology

Ref: Author.

On the other hand, in Figure 34 shows a more detailed view of the surface morphology of the coatings. The coating M02 presented a more faceted surface, but with a larger number of voids, which in turn might contribute to worse mechanical properties. The features on coating M03 are more rounded; meanwhile M01 presents a mixture of the previous two.

The samples were subjected to XRD analysis for phase identification and to determine the texture coefficient. The diffractograms are exhibited in Figure 35, as well as the analysis of texture coefficient.

Figure 35 - XRD for different concepts showing the formation of CrN phase

Ref: Author.

It is possible to observe that the peaks are matched to the ones expected for the formation of CrN. No peaks of Cr_2N or AlN were found, which confirm the presence of aluminum as a substitutional element without phase segregation or the formation of AlN precipitates. A small shift to the left was found for all peaks, towards smaller 2θ . This can be attributed to the presence of compressive residual stresses on the plane parallel to the surface, which in turn leads to a Poisson expansion in the direction perpendicular to the surface. Furthermore, the analysis of the texture coefficient showed a strong texture on the (200) plane.

The presence of satellite peaks was analyzed and by using Eq. 16 and Eq. 6 the periodicity was estimated and calculated from the X-Ray diffractograms, respectively. The results are shown in Table 6.

Table 6 - Estimated and calculated values for periodicity

<i>Periodicity</i>	M01	M02	M03
<i>Estimated [nm]</i>	10,5	9,5	8,7
<i>Calculated by X-Ray [nm]</i>	-	7,1	7,7

Ref.: Author.

No satellite peaks were found in the sample M01, which might indicate the absence of a multilayered structure. The results for calculated and estimated periodicity were not too far apart, which indicates that the X-Ray method is also a valid one for analysis.

AFM images for all the coatings are presented in Figure 36 and the results of the different roughness parameters are shown in Table 7.

Figure 36 - AFM images showing topography features

Ref: Author.

The AFM images confirm the analysis made from the SEM images. The M03 sample has bigger and rounder grains; meanwhile M02 has the faceted structure. Thus, it is possible to quantify the features observed in the SEM images by means of the AFM image, which accurately represents the coating surface.

Table 7 - Roughness values from AFM measurements

<i>Sample</i>	<i>Ra [nm]</i>	<i>Skewness</i>	<i>Max Peak [μm]</i>
M01	120.3	0.20	1.14
M02	186.7	0.23	1.82
M03	183	0.68	1.83

Ref.: Author.

The results from AFM measurements showed lower surface roughness for M01 sample. This sample also had the lowest value of maximum peak of the three samples. The more positive value for the skewness of M03 indicates an asymmetrical distribution, which in turn determines that there are higher peaks.

Nanohardness measurements were carried out in all three samples. The results can be observed in Figure 37.

Figure 37 - Nanohardness tests showing higher values for Concept M03

Ref: Author.

Results of nanohardness test showed higher values for the M03 sample. The samples M02 and M03 had the highest number of CrAl targets operating and it is known that CrAlN coatings are usually harder than CrN coatings (BARSHILIA *et al.*, 2006). Thus, this might justify the lower value found for M01 coatings. On the other hand, M03 coatings had one target of CrAl connected to a HiPIMS power source, which in turn produces harder coatings. This contributed to higher hardness of the multilayer structure. No superlattice hardening effect was found in any of the samples, which indicates that a mixture rule for hardness might be related to all results found so far.

Wear tests were performed to evaluate the behavior of the coatings during contact against the cylinder liner and the results are shown in Figure 38.

Figure 38 - Wear test results showing lowest wear for sample M03

Ref: MAHLE (Adapted, 2018).

The wear test showed higher wear for the sample M02, which was the one without base layer. The total measured wear was high enough to indicate the total coating removal during the test. This corroborates the importance of the base layer under high load application. The coating detachment probably led to the third body formation, which further increased the wear of the coating. M03 wear was significantly lower than the other samples. This result can be justified for the higher hardness of this coating as well as a favorable surface roughness profile.

Based on the results of hardness and wear, the third concept (M03) was chosen to be studied. It was the concept with higher hardness and lower wear rate. Although it was the hardest coating, the values were far from what was expected for multilayer coatings (BARSHILIA *et al.*, 2007; KIM, BYUN and HAN, 2009). Therefore, an intermediate stage was proposed in which the effect of bias was explored.

6.2. SECOND STAGE – TESTING SUBSTRATE BIAS INFLUENCE

Three substrate bias values were proposed: -120V (the same used on the first step), -150V and -180V. Furthermore, a change of base layer was studied to provide further increase on adhesion of the coating to the substrate. A base layer of CrAlN was produced with the deposition parameters for both base layer and coating as shown in Table 8.

Table 8 - Deposition parameters for the second set of samples

Bias [V]	-120	-150	-180
Carousel Speed [rpm]	1.0	1.0	1.0
Base Layer	CrAlN		
Base Layer Deposition Time [hrs]	4		
Target (Base layer)	CrAl HiPIMS + CrAl DC		
Atmosphere Base Layer [sccm](gas)	50 (N ₂) + 40 (Ar)		
Target (Coating)	CrAl HiPIMS + CrAl DC + Cr DC		

Ref.: Author.

An SEM image of the fracture of the coatings is shown in Figure 39. It is possible to observe that the coating with the bias of -120V have more intercolumnar pores and voids and that these features tend to disappear as the negative substrate bias is increased to -150 and -180V. On the latter, the spaces between columns are almost imperceptible. The contribution of increasing bias as a mean to provide better densification is well described when considering that more energy is given to the arriving atoms for higher bias values, thus enhancing adatom mobility and providing coating densification.

Figure 39 - Fracture of the rings showing the influence of bias on the morphology

Ref.: Author

The total thickness of the coating is exhibited in Table 9. Results show that the coating total thickness was increased as the bias was varied from -120V to -180V. According to the model proposed by Anders (2010), as the bias is increased and the coating gets denser, a decrease in coating thickness is expected. This is the opposite fact that is observed here. One possible explanation is that these three coatings were produced sequentially (the first coating was produced with -180V, then the next with -150V and finally the last with -120V) and a full cleaning of the deposition chamber was not performed between the depositions. As CrN is an insulating material, there is a reduction on the process efficiency, thus leading to a reduction of the deposition rate, which is not necessarily attributed to the increase in bias.

Table 9 - Measured coating thickness as a function of bias

		-120V	-150V	-180V
Thickness [μm]	<i>Total</i>	9.5±0.1	10.1±0.1	10.3±0.1
Dep. Rate [μm/hr]	<i>Base layer</i>	0.23	0.25	0.35
	<i>Coating</i>	0.41	0.43	0.46

Ref.: Author

The difference of deposition rate is rather small, but total thickness changes due to the duration of the process (20 hours).

Top morphology was also evaluated and it can be observed in Figure 40. The reduction of the voids between the grains as bias value is increased is clearly seen from this image, confirming the analysis made from the previously shown fracture image. The rounded features observed from M03 coatings are still present, although it is possible to observe a few faceted grains, mostly on the coating with -120V.

Figure 40 - Top image showing changes on the morphology as the negative bias is increased

Ref: Author.

The XRD results, in Figure 41, confirmed the formation of the CrN phase regardless of the applied bias. Results also present the satellite peaks near the (311), which will be used to calculate the periodicity of the coatings. The results of these calculations, as well as the expected values estimated by Eq. 16 are presented in Table 10.

Figure 41 - XRD results as a function of bias

Ref: Author.

The texture coefficient showed preferential growth for the (200) plane, regardless of the utilized bias value. This behavior is quite different from what can be found in the published paper that utilized the same PVD deposition chamber to produce CrN monolayer coating. In it, the texture coefficient changed as a function of the bias values, and for higher bias, the (220)

was the preferred orientation for HiPIMS coatings produced with a frequency of 500Hz. Meanwhile, DC coatings presented (111) texture (GUIMARÃES *et al.*, 2018). This might indicate that the presence of a multilayer structure and the continuous rotation of the substrate inhibit the growth for other directions.

The values presented in Table 10 show good agreement between the expected and calculated values of periodicity. Furthermore, as the deposition rate was lower for these set of samples when compared to the previous set, so was reduced the periodicity, since the latter is closely dependent to the former. Moreover, almost no difference was observed in the periodicity as the bias values was varied.

Table 10 - Results of the calculated and estimated periodicity

<i>Periodicity</i>	-120V	-150V	-180V
<i>Estimated [nm]</i>	7.6	7.6	7
<i>Calculated by X-Ray [nm]</i>	10.1	7.7	8

Ref.: Author.

Figure 42 presents the 3D representation of the AFM measurements of the coating. Meanwhile, Table 11 summarizes the values found during the analysis.

Figure 42 - AFM images of the coatings with bias variation

Ref: Author.

The AFM image shows that the increase of bias lead to a more uniform surface, even though the roughness (Ra) is higher. This can be confirmed when observing the calculated skewness. The -180V sample presents the lowest skewness, close to zero. Thus, this indicates the presence of a distribution of values close to the normal distribution, which means that it has approximately the same amount of valleys and peaks. It is also possible to observe a cone-like defect on the -180V coating, which contributed to a higher roughness value for this coating.

Table 11 - Roughness results as function of applied bias

<i>Bias [-V]</i>	<i>Ra [nm]</i>	<i>Skewness</i>	<i>Maximum [μm]</i>
<i>120</i>	102.1	1.22	1.392
<i>150</i>	98.3	0.59	1.509
<i>180</i>	118.9	0.161	1.434

Ref.: Author.

Hardness tests were conducted for the samples produced in this stage and the results are shown in Figure 43. The hardness value decreased as the bias was increased, with a peak of 22 ± 2 GPa for -120V and 19 ± 2 GPa for -180V.

Figure 43 - Nanohardness test showing constant decrease of hardness as the bias value was increased

Ref: Author.

The torsion test was applied for these samples (Figure 44) and coatings with -150 and -180V failed during it, indicating poor adhesion to the substrate. The causes of this failure are

probably related to using of a CrAlN base layer. The use of bias increases the hardness but also the residual stresses of the coatings (GUIMARAES *et al.*, 2018). We suspect that the failure started on the base layer due to the presence of high levels of residual stresses. Then, it propagated through the coating, leading to the full delamination of it when the torsion was applied.

Figure 44 - Torsion test showing delamination of the coatings for higher bias values

Ref: Author.

With the failure of the coatings, they were not subjected to the wear test. Thus, a new set of samples was proposed (third stage) to evaluate if the failure was caused by the stresses on the coating due to the high bias values or the nature and stresses present on the base layer.

6.3. THIRD STAGE – TESTING BASE LAYER COMPOSITION

For this stage, all parameters were kept the same, except for the target (Cr instead of CrAl) and the N₂ flow was turned off. These changes can be observed in Table 12, which summarize the deposition parameters.

Table 12 - Deposition parameters for the third stage of coating deposition

Bias [V]	-120	-150	-180
Carousel Speed [rpm]	1.0	1.0	1.0
Base Layer Deposition Time [hrs]	2		
Target (Base layer)	Cr		
Atmosphere Base Layer [sccm](gas)	40 (Ar)		
Target (Coating)	CrAl HiPIMS + CrAl DC + Cr DC		

Ref.: Author.

The SEM images of the three coatings are presented in Figure 45. As in the previous stage, the reduction of voids between the grains is observed as the bias is increased, which indicates a better coating densification and which is predicted by the model proposed by Anders. Apparently, the full dense, glassy structure which can be produced by HiPIMS, cannot be achieved by means of increasing bias. This can be explained by the presence of two DC power source, which contribute in a significant way to the coating deposition, since they have higher individual deposition rate than the single HiPIMS employed in this study.

Figure 45 - Morphology of the coating's fracture

Ref.: Author.

From Table 13 it is possible to observe that, differently from the previous stage, no significant difference was found for coating thickness and deposition rate as the bias was increased.

Table 13 - Thickness measurement for different bias values

		-120V	-150V	-180V
Thickness [μm]	<i>Total</i>	9.1 $\pm$ 0.2	9.1 $\pm$ 0.1	9.2 $\pm$ 0.2
Dep. Rate [$\mu\text{m/hr}$]	<i>Base layer</i>	0.37	0.34	0.23
	<i>Coating</i>	0.42	0.42	0.44

Ref.: Author.

Figure 46 - Top morphology changes as the negative bias is increased

Ref: Author.

The same result of coating top morphology is observed here and in the previous step, the reduction of the voids between the grains indicating the coating densification. This is quite expected, when one evaluates the model proposed by Anders (2010). As the energy of the arriving ions and neutrals increase, more movement they have at the surface, thus enhancing coating densification.

The diffractograms for all samples produced in this stage is presented in Figure 47, together with the texture coefficient evaluation.

The results from Figure 47 (A) shows that regardless of the bias voltage, only the phase related to the CrN is present. Once again, no peaks of AlN were found, indicating that the aluminum is acting as a substitution element on the crystalline structure. It is also possible to observe that the peaks are shifting more to the left, towards smaller 2θ values, which in turn indicates the presence of an increasing residual stress as the bias is also increased. In Figure 47(B), it is evident the predominance of the (200) peak when compared to the other ones by the calculation of the texture coefficient.

From the results of the diffractograms the periodicity was calculated. Meanwhile, from SEM images of the fracture, the periodicity was estimated by using Eq. 16. The results are shown in Table 14.

Table 14 - Estimated and calculated periodicity for different bias levels

<i>Periodicity</i>	-120V	-150V	-180V
<i>Estimated [nm]</i>	7	7	7.3
<i>Calculated by X-Ray [nm]</i>	7.7	7.4	10

Ref.: Author.

The results are quite close to each other especially for -120V and -150V. The higher deviation for -180V could be caused by the presence of higher residual stresses, which dislocated the analyzed peak and could contribute to measurement error.

AFM images were produced to evaluate roughness parameters and they are exhibited in Figure 48. Furthermore, Table 15 presented the values of R_a , skewness and maximum peak for all the samples produced in this stage.

Figure 48 - AFM images for different bias

Ref.: Author.

In this stage, almost no difference in coating morphology was found for the different bias values, especially when analyzing the samples with -120V and -150V. This can be confirmed by analyzing the values found in Table 15. The results show an increase in roughness as the bias was increased, possibly lead by the presence of a defect in the evaluated region of the -180V sample. Furthermore, the presence of the maximum of 1.65μm for this sample evidences the presence of the defect, which can also be observed on the light region of the figure. The small values of skewness can be read as a uniformity of the coating, since values close to zero represents a uniform distribution of valleys and peaks.

It is important to highlight the different behavior of the roughness when compared to the previous stage. It is known that thin film growth is closely related to the conditions of growth. Thus, as the coatings have different base layers (CrAlN for the Second Stage and Cr

for the Third Stage), different conditions might be imposed to the film, thus leading to different surface features.

Table 15 - Results of roughness by AFM images

<i>Bias [-V]</i>	<i>Ra [nm]</i>	<i>Skewness</i>	<i>Maximum [μm]</i>
<i>120</i>	101.4	0.22	1.05
<i>150</i>	110.1	0.18	1.06
<i>180</i>	144.9	0.14	1.65

Ref.: Author.

Hardness tests were performed in all samples produced in this stage and the results are shown in Figure 49. Higher hardness was found for the coating produced with -150V and meanwhile the values of -120V and -180V were approximately the same. The huge dispersion of results for -180V can be justified by the presence of higher roughness and higher amount of defects. The nanohardness test is a technique extremely sensitive to surface features and even after polishing the samples it is not possible to guarantee uniformity to the surface. The cone-like defects, when polished, often leave as a whole piece of coating and they leave behind a hole in its place. As the evaluation of hardness is performed in this surface, a higher dispersion of results can be found.

Figure 49 - Hardness test as a function of negative substrate bias

Ref.: Author.

The wear test results, both for the coatings and for the cylinder liner, is presented in Figure 50. The results showed an increased performance of the coating with -150V.

Furthermore, the results presented higher dispersion for the -180V coating. This is directly related to the reasons presented in the last paragraph. As the cone-like defects leave the coating, it enters the region of wear as a third body. Since they are as hard as the original coating, this accelerates the wear degradation of the coating.

Figure 50 - Wear results for coatings under different bias levels

Ref.: MAHLE (Adapted, 2018).

The results of wear and hardness indicate that the best condition for evaluate the influence of periodicity is with -150V. Although the hardness test is inconclusive to some degree, due to the presence of high deviation, the wear test corroborate this result. Thus, the next stage is proposed to evaluate the influence of the carousel speed and thus of the coating periodicity on the structure, morphology and properties of the coating.

6.4. FOURTH STAGE – EVALUATION OF THE PERIODICITY INFLUENCE

After evaluating the results of wear and nanohardness, the final stage of this study consists in the production and characterization of the coatings under different carousel speed. The parameters for this stage are shown in Table 16.

Table 16 - Deposition parameters for the fourth stage

Bias [V]	-150	-150	-150
Carousel Speed [rpm]	0.5	1.5	2.0
Base Layer Deposition Time [hrs]	2		
Target (Base layer)	Cr		
Atmosphere Base Layer [sccm](Gas)	40 (Ar)		
Target (Coating)	CrAl HiPIMS + CrAl DC + Cr DC		

Ref.: Author.

SEM images of the fractured coating were made (Figure 51) to observe morphology and for coating thickness measurements. It is possible to observe that the coating produced with 1.5rpm presented thicker coatings meanwhile the other two (0.5rpm and 2rpm) presented similar values. Not only that, but the deposition rate of the base layer is also higher for the sample with 1.5rpm. This might indicate that this carousel speed can be optimal for increasing the coating deposition rate.

Figure 51 - Fracture of the coatings produced under different carousel speed

Ref: Author.

Table 17 - Results of the thickness measurement as a function of the carousel speed

Carousel Speed [rpm]		0.5	1.5	2.0
Thickness [μm]	<i>Total</i>	10.5 $\pm$ 0.1	12.1 $\pm$ 0.1	11.1 $\pm$ 0.2
Dep. Rate [$\mu\text{m/hr}$]	<i>Base layer</i>	0.34	0.63	0.34
	<i>Coating</i>	0.53	0.61	0.56

Ref: Author.

Based on Eq. 16 for the periodicity estimation, it was possible to calculate the effects of the carousel speed variation on the periodicity. As predicted by the equation, the behavior of the periodicity was supposed to be a function of the carousel speed responded as a function such as $y = ax^{-1}$. Thus, the periodicity was plotted versus the speed and the result is shown in Figure 52.

Figure 52 - Estimated periodicity as a function of the carousel speed

Ref: Author.

A curve linearization was produced to calculate the value for the constant, as depicted in Figure 53. An important conclusion is that the fit indicates that an constant average deposition rate can be found and equal to $0.51 \pm 0.03 \mu\text{m/hr}$, regardless of the speed. Minor variations can be found, but are a result of the conditions of the deposition, such as sample preparation and/or cleanliness of the deposition chamber.

Figure 53 - Linearization and fit of the curve Periodicity vs Carousel Speed

A detailed image of the sample produced with 0.5rpm is shown in Figure 54. This was the coating produced with the lowest speed and it presents the higher periodicity. Thus, a successful attempt to observe the multilayer structure was made. The yellow highlight the place where the multilayer structure can be observed. Furthermore, the black box on the top left corner represents a Fast Fourier Transform of the region. The measurement of the spots present a value of 17.25nm, indicating the presence of a periodic structure.

Direct measurements on the yellow region also show that the periodicity in this image is 17.3nm, meanwhile the estimated value from Eq 16 and plotted in Figure 52 is 17.5nm. This result confirms the validity of the equation to estimate the periodicity of the processes used so far.

Thus, two possibilities are raised as why these multilayers cannot be observed as the periodicity is reduced. The most plausible explanation is that the microscope does not have enough resolution to make these images under these conditions. The contrast of the BSE signal from CrN and CrAlN might not be enough to differentiate the multilayer, which would lead to an erroneous interpretation for the absence of multilayer structure.

Another possibility is that, as the periodicity is reduced, it becomes easier for the aluminum to diffuse in the layers of CrN around the layers of CrAlN, thus creating a monolayer of CrAlN with nanograins (WASA, KANNO and KOTERA, 2012). To guarantee which is the right interpretation of this phenomenon, the use of Transmission Electron Microscopy and/or Scanning Transmission Electron Microscopy is recommended.

Figure 54 - Cross section image showing the presence of periodic structure

Ref: Author.

Previous studies characterized a coating deposited under different conditions and with different source combination. This was a preliminary study that was performed in September/2016 to check the feasibility of our deposition chamber producing multilayer coatings. This sample was taken to Saarbrücken, Germany, where it was analyzed with a Scanning Transmission Electron Microscope. The result is shown in Figure 55.

Figure 55 - Comparison of a)SEM and b)STEM images of the same coating

Ref: Author.

Figure 55 presents a comparison of a SEM (EESC-USP) and a STEM (Germany) image of the same coating under different magnifications. From Figure 55(A) it is not possible to observe the presence of any multilayer structure. Furthermore, it is possible to observe that the image is blurred, which is a result of interference from external magnetic field. Any attempts to increase the magnification would result in an interference increase. Meanwhile, the Figure 55(B) clearly shows the multilayer. The periodicity in this example was 3.4nm and, by using the Eq. 16, the estimated periodicity value for this coating was 3.7nm, which again indicates good agreement between predicted and measured periodicity.

Thus, this fact reinforces the interpretation that, for lower periodicities, it is not possible to observe the multilayer structure due to limitations of the microscope.

The top SEM images of the coatings produced in this stage are shown in Figure 56.

Figure 56 - Top SEM image as a function of the speed

Ref: Author.

Top morphology evaluation showed almost no difference regarding the shape of the grains as a function of the periodicity. Nevertheless, a great increase of defects was found for the coating produced at 1.5rpm, as 3.6% of the coating surface area was formed by defects. This was severely reduced for 0.5rpm (0.7%), which can be observed in Figure 57. To count these defects, only the nodular and cone-like defects with an area higher than $20\mu\text{m}^2$ were taken into consideration. According to Biswas *et al.* (2017), these defects are originated by impurities present in the deposition chamber such as dust and flakes from the walls. Furthermore, they proved that the amount of the area occupied by defects is influenced by changing the pressure (BISWAS *et al.*, 2018a) and bias (BISWAS *et al.*, 2018b).

Figure 57 - Evaluation of the area and mean size of defects as a function of the speed

Figure 58 presents the results of the X-Ray Diffraction (A) and the results of the texture analysis (B). The strong texture is present on (200) and the texture coefficient for other peaks were really low (0.008 in general).

Figure 58 - XRD results from carousel speed variation

Results from periodicity evaluation can be found in Table 18. The results show satisfactory agreement from the estimated values, except for the 0.5rpm coating. This might be caused by the convolution of the main peak and the satellite. This could have led to some small degree of error when deconvoluting the curve and the error was propagated to the periodicity

value. Nevertheless, both results show the same trend of reduction of periodicity for higher values of carousel speed.

Table 18 - Estimated and calculated results from XRD for periodicity variation

<i>Periodicity</i>	0.5rpm	1.5rpm	2.0rpm
<i>Estimated [nm]</i>	17.5	6.7	4.6
<i>Calculated by X-Ray [nm]</i>	12.7	6.9	5.4

Ref.: Author.

Results from AFM measurements and the 3D representation of coating top morphology are presented in Table 19 and Figure 59, respectively.

Figure 59 - AFM images of coatings produced with different carousel speed

Ref: Author.

Table 19 - Roughness results of the samples made with different speed

<i>Carousel speed [rpm]</i>	<i>Ra [nm]</i>	<i>Skewness</i>	<i>Maximum [μm]</i>
0.5	85.23	0.336	0.90
1.5	101.53	0.241	0.84
2.0	190.75	0.628	1.93

Ref: Author.

The results of nanohardness test are shown in Figure 60. These results show that the hardness value for all coatings is somewhat independent of the periodicity variation and oscillated around 23GPa. The highest value was found for 0.5rpm and 17nm (25 ± 4 GPa) and the lowest for 1rpm and 7nm (22 ± 3 GPa). Nevertheless, the results agree with the studies conducted by Bobzin *et al.* (2016), which presented values from 23.9 GPa for a similar hybrid process. They showed that, for a hybrid process, the hardness can be given by a combination of the hardness of the different processes. On the other hand, Barshilia *et al.* (2007) presented results of increased hardness by changing periodicity for a CrN/CrAlN deposited by dcMS, reaching 30GPa for 7nm periodicity.

Figure 60 - Hardness test showing independence of carousel speed.

Ref: Author.

The behavior on the wear test due to the periodicity change is shown in Figure 61.

Figure 61 - Wear test results from periodicity variation

Ref.: Author.

It is possible to observe that no significant difference is observed in terms of total wear for the different coatings in this stage. There is some degree of variation on the dispersion of the results, with the samples with lower hardness showing less dispersion. Furthermore, the sample with the highest carousel speed is the one with lower average wear.

The curves of corrosion tests and the calculated results, by means of the Tafel Extrapolation Method are shown in Figure 62 and Table 20, respectively.

Figure 62 - Polarization curves for different carousel speed

Ref.: Author.

Table 20 - Results of the corrosion test

	0.5 rpm	1.0rpm	1.5rpm	2.0rpm
E_{corr} [mV]	-108.06	-120.11	-86.82	-120.12
I_{corr} [$\mu A/cm^2$]	38.08	23.43	13.73	20.74

Ref.: Author.

Differently of what was found by Biswas *et al.* (2018b), the coating with more defects presented here the higher corrosion resistance. Of course there are other mechanisms in play. The periodicity decrease is described to increase the corrosion resistance of materials, since the different layers act as barriers for the corrosion media to arrive in the subsequent layer. This can be verified up to 1.5rpm (6.7nm), but the results of 2rpm (4.6nm) contradicts this trend. However, this same trend is observed for the superhardening effect. The hardness is increased up to 5nm and then falls down to lower values, which is exactly what was observed from our corrosion data. Another possible explanation for the lower corrosion resistance is the presence of higher roughness (roughness from the 2rpm coating is almost twice the one for 1.5rpm).

7. CONCLUSIONS

The necessity to improve the wear behavior of piston rings was the main motivation that drove this research. Current mechanical and thermal solicitations for the rings are severe and a new solution was required. PVD coatings, especially the ones produced by HiPIMS showed promising results for low wear-high hardness applications.

In this study, four main variables were studied by using a PVD chamber equipped with a HiPIMS and two DC power sources. Firstly, it was necessary to define which combination of target material and power sources could provide the best results in terms of wear and hardness. The results showed that a combination of CrAl with HiPIMS, CrAl with DC and Cr with DC provided the best results, but hardness values were lower than expected.

Then, an intermediate step was proposed to enhance coating hardness by increasing bias values. The base layer was produced with CrAlN, which proved to fail under the torsion test due to high residual stress on the base layer, especially for higher bias. Therefore, a third step was required, in which a base layer of Cr would allow utilizing these high bias levels.

As a result, the coating produced with -150V presented higher values of hardness and an improved wear behavior with the lowest dispersion of results, suggesting that this level of bias was an optimized solution to explore the effects of the periodicity change. Furthermore, an intermediate roughness was found for this coating, and a reduced number of defects, which are possible explanations for the higher wear resistance of the coating.

Finally, three different speeds of the carousel were used to produce coatings with different periodicity. The superhardening effect could not be found for these coatings, but an increase in corrosion resistance, especially for 1.5rpm was found. For wear, we found no trend as a function of the periodicity. Nevertheless, all wear results are lower than the one found in the commercial coating, which contributes to the understanding that a multilayer coating contributes to a higher wear resistance.

For all coatings, the preferred orientation growth was found to be on the $\langle 200 \rangle$ direction, with high values of texture for these planes.

The results showed that CrN/CrAlN multilayer coatings provided high hardness and great wear and corrosion resistance and it is a viable solution for piston ring application.

8. SUGGESTIONS FOR FUTURE WORKS

This study intends to be a first exploration of multilayers coatings developed at the EESC-USP. Thus, there is still plenty of room for improvements and further analysis of the coatings.

Regarding the deposition process, it is suggested examining of the influence of different parameters that were kept constant during this study, such as pressure, flow rate of argon and nitrogen, as well as the evaluation of different pulse times (both on and off). Furthermore, the study of different aluminum content on multilayer coatings should provide results toward the increase of the mechanical properties of the coatings.

Still regarding the process, it is important to have tools and equipment that provide in situ diagnostics of the deposition process. This would greatly enhance the capabilities of the coating deposition and significant results could be found.

The use of Transmission Electron Microscopy as an additional tool for the multilayer/superlattice determination and visualization could be also a possible test to confirm the presence of the multilayers. The SEM, although a versatile technique, lacks the resolution to provide clear images in such small scales.

The PVD deposition chamber installed at EESC-USP is a versatile equipment and provide the opportunity to develop several studies with different conditions and materials for a wide range of applications.

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