Development of Accident Tolerant Fuel Cladding via Magnetron Sputtering Chromium Depositions for Light Water Reactors

> THAIS RACHID NETTO PhD 2024

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A thesis submitted in partial fulfilment of the requirements of Manchester Metropolitan University for the degree of Doctor of Philosophy

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Declaration

This is to certify that the material contained in this thesis has been produced by author and has not been accepted in substance for any other degree and is not currently submitted in candidature for any other academic award.

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Abstract

Since the Fukushima accident, much research has focused on developing accident-tolerant fuels (ATF) to use in Light Water Reactors (LWR) to enhance the safety of the existing zirconium alloy fuel rods. Replacing or coating the zirconium (Zr) alloys have been considered as part of the solution for this problem. Fretting wear during normal operation is a major concern to the nuclear industry. Fuel rods in a nuclear reactor experience coolant flow induced movement against the support grids, known as grid-to-rod fretting (GTRF), which can lead to failures under normal operating to their premature removal.

Chromium-based coatings applied to the fuel rods have shown improved results regarding oxidation and mechanical resistance under the normal working conditions of the LWR. The deposition technology used for these coatings is important because it directly affects the coating performance. Therefore, in search of high quality and dense films, the magnetron sputtering technique was chosen for this project.

The coating technique should also guarantee characteristics similar to those of the original zirconium rods, such as wettability. Wettability is a crucial parameter that significantly impacts heat transference inside the reactor. Surface roughness can substantially influence the wettability of surfaces. Therefore, understanding the influence of roughness on coating wettability is an essential achievement regarding the new approaches to creating a safer ATF.

Therefore, this work aims to produce Cr and CrN coatings for Zr alloy nuclear fuel rod cladding material with enhanced mechanical resistance using magnetron sputtering. Additionally, we aim to analyse the bias voltage parameter to optimize the coating wear resistance. Furthermore, we aim to determine the impact of substrate roughness on the wettability of Cr coatings.

To achieve these aims, Zr alloy substrates were coated using unbalanced magnetron sputtering in an argon environment in a pulsed DC mode with varied coating parameters, such as bias and deposition time. The coating structures and characteristics were analysed by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), white light optical profilometry (WLP), and the wettability was assessed using a contact angle goniometry. In addition, the mechanical properties

of the coating as hardness and elastic mode were analysed using a nanoindenter, the adhesion to the substrate was tested with a scratch test and the friction test to mimic the GTRF was performed in a tribometer.

Overall, the results show that while the Cr coatings preserved substrate roughness, surface roughness alone had minimal influence on wettability, suggesting surface chemistry plays a more dominant role in hydrophobic behaviour. In optimizing coating parameters, thicker Cr coatings—particularly those exceeding 6 µm—significantly improved wear resistance, with bias voltage impacting coating performance. The Cr coating deposited for 6 hours at -50V bias provided the best wear resistance, although with lower adhesion and higher cracking. Conversely, the -100V bias coating offered superior adhesion and crack resistance but lower wear protection. The CrN and Cr+CrN coatings demonstrated poor adhesion, toughness, and no wettability advantage over Cr coatings, making them less practical for ATF applications. Overall, Cr coatings with optimized thickness and bias voltage present a more effective and manufacturable solution for enhancing the performance of Zr-based ATF cladding.

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Nomenclature

AE – Acoustic emission INL – Idaho National Lab **AFM** – Atomic force microscopy LOCA – Loss of cooling accident **AIP** – Arc ion plating **LWR** – Light water reactors **ASTM** – American Society for Testing MCT – Micro combi tester and Materials **MFM** – Magnetic force microscopy **ATF** – Accident tolerant fuel MIT – Massachusetts Institute of **BCC** – Body centred cubic Technology **BWR** – Boiling water reactors MPa – Megapascal **CHF** – Critical heat flux **NBA** – no applied bias **CMC** – Ceramic matrix composite **PD** – Penetration depth **COF** – Coefficient of friction **PWR** – Pressurized water reactors **CS** – Cold spray **RF** – Radio frequency **CTE** – Coefficient of thermal expansion **RFMG** – Radio frequency magnetron **CVD** – Chemical vapour deposition sputtering **DBA** – Design basis accidents **RT** – Room temperature **DC** – Direct current **SEM** – Scanning electron microscopy **EBSD** – Electron backscatter diffraction **SPM** – Scanning probe microscopy transmission **EDX** – Energy dispersive X-ray STEM Scanning _ spectroscopy electron microscopy **EFM** – Electric force microscopy **STM** – Scanning tunnelling microscopy **EIT** – Elastic modulus SZM – Structure zone model FIB-SEM Focused ion beam-TEM Transmission electron scanning electron microscopy microscopy **FIV** – Flow-induced vibration **UWM** – University of Wisconsin at **GPa** – Gigapascals Madison VCU **GTRF** – Grid-to-rod fretting _ Virginia Commonwealth Impulse HIPIMS _ High-Power University Magnetron Sputtering **WLI** – White light interferometry **HIT** – Indentation hardness **XRD** – X-ray diffraction

I. Background and context

Chapter 1. Introduction

The greenhouse effect is a critically important problem to be monitored. One of its main causes is the large amount of carbon dioxide (CO₂) released by energy generation from fossil fuels. Nuclear energy may be an option to reduce this problem since it does not release CO₂ into the atmosphere¹. However, the serious accident at Fukushima Daiichi in 2011 highlighted the vulnerabilities of current fuel designs under severe accident conditions. In this accident, a loss of coolant drastically increased the temperature inside the reactor, as a result the fuel cladding tube started to suffer physical and chemical degradation².

Light water reactors (LWRs) represent the majority of reactor designs in operation globally and a key component in these reactors are the fuel cladding, which acts as the primary barrier between the radioactive fuel and the reactor environment³. Traditionally, zirconium-based alloys have been employed as material for the fuel cladding in LWRs. Zr alloys were selected due to a combination of resistance to neutron irradiation, low absorption of thermal neutrons, and reasonable corrosion resistance in a water environment at normal reactor conditions⁴. However, Zr alloys could not withstand the extreme conditions generated by the loss of cooling accident (LOCA). The resulting steam atmosphere and high temperatures caused rapid Zr oxidation and the resultant reactions released hydrogen and, in addition to the material's degradation, an explosion occurred at the Fukushima plant^{2,5}.

Moreover, the failure of cladding rods is a problem in daily operation for uncoated cladding in LWRs. A study showed that about 65% of fuel rod failures were caused by the phenomenon called grid-to-rod fretting⁶. The fuel rod inside the reactor is held by a grid and the water flow inside the reactor induces a vibration between the grid and the fuel tube. This repeated movement for long time periods causes a gradual relaxation of the grid, increasing the gap between the cladding and the grid^{7–11}. The main concern is that the nuclear rod can be damaged and may lead to leaks, where the radioactive fission gases from the fuel could escape, leading to a radioactive accident.

Therefore, these both issues have prompted the development of accidenttolerant fuels (ATF)¹². Two possible solutions are being considered. Firstly, replacing the Zr alloy cladding entirely with a more oxidation resistant material. Secondly, coating the exterior of the existing Zr alloy cladding with a thin layer of an alternate material to protect the Zr alloy from oxidation in high temperature steam. Coating of the existing Zr alloy cladding to enhance its performance is seen as a promising short-term solution¹³. An effective coating onto the Zr alloy must resist oxidation in high-temperature steam leading to a decrease of H₂ release, improve fission product retention and improve mechanical strength at high temperatures¹³. To achieve this, it is essential that the coating presents a similar coefficient of thermal expansion (CTE) and melting point to the substrate, as well as chemical compatibility during the coating material should not impair the cooling efficiency of the nuclear rod in normal operation. Therefore, to study the effect of the surface roughness and chemistry with the contact angle is relevant when it comes to efficient cooling of the rods¹⁴.

Some studies have shown that Cr-based coatings for Zr alloys show improvements in ATF performance. Chromium exhibits properties that make it a good candidate⁵. For instance, the Cr melting point is similar to that of Zr, both materials have a similar CTE, and Cr forms a passive oxide film (Cr₂O₃) at high temperatures, which protects the Zr alloy from corrosion, increases the mechanical resistance, and it is significantly more stable in LOCA conditions^{15–18}. There is also evidence that chromium nitride (CrN) is a competitive candidate for coating Zr alloys. This ceramic material is brittle, hard, has excellent thermal properties, and is resistant to oxidation^{19,20}.

Several technologies may be used for thin film deposition on substrates, each one offers coatings with different characteristics that imply distinct performances. Magnetron sputtering is a physical vapour deposition (PVD) technique, providing coatings with properties desired for nuclear rod cladding application, for example, adherent, dense and homogenous coatings²¹.

Most of the current literature on Cr-based coatings using magnetron sputtering focuses on optimizing deposition parameters, such as bias voltage, to improve the oxidation behaviour^{22,23}. Other studies primarily concentrate on the variation and enhancement of wear test parameters for Cr-based coatings^{24,25}.

Therefore, this project investigates the development of accident-tolerant fuel cladding via magnetron sputtering of chromium coatings onto zirconium alloys. As

a novel approach, this study focuses on optimizing the deposition parameters to achieve desirable coating characteristics to mitigate the fretting wear and to enhance the performance of nuclear fuel rods. Furthermore, the current literature lacks studies on the influence of roughness on the wettability of Cr-based coatings produced by magnetron sputtering. Thus, this investigation also focuses on the influence of substrate roughness on the wettability of chromium coatings. Subsequently, the influence of bias voltage and deposition time on the properties and the mechanical performance of Cr and CrN coatings will be assessed.

1.1 Research Aims

The primary aim of this project is to develop an ATF cladding that can enhance the safety and reliability of LWRs, specifically by reducing the risk of cladding failure during normal operation and under accident conditions.

Therefore, this project aims to deposit Cr-based coatings to zirconium alloy fuel rod cladding using magnetron sputtering, with the goal of improving mechanical performance and mitigating grid-to-rod fretting (GTRF) during reactor operation.

1.1.1 Research Objectives

- Investigate the effect of substrate surface roughness on the wettability of Cr-coated samples and evaluate its potential role in enhancing critical heat flux (CHF) performance.
- Optimize magnetron sputtering parameters—specifically bias voltage and deposition time—for the deposition of Cr-based coatings, including pure Cr and CrN variants, to enhance their structural integrity, chemical stability, and mechanical properties such as wear resistance and scratch performance.
- Perform physicochemical characterisation of the coatings (e.g., microstructure, composition, roughness, hardness, and wettability) to establish correlations between processing parameters and coating performance.

4. Conduct friction wear tests to simulate the GTRF phenomenon and determine the optimal coating parameters that provide the best wear resistance.

Chapter 2. Literature review

2.1 Zircaloy-based fuel cladding in light water reactors (LWR)

In this section of the work, several key themes surrounding Zircaloy-based fuel cladding in Light Water Reactors (LWRs) will be discussed. Firstly, an overview will be presented of the importance of nuclear power and its basic concepts, including nuclear fission and reactor operation, to establish a foundation for understanding the role of fuel cladding. Following this, the characteristics and composition of zirconium alloys used as fuel claddings will be discussed, focusing on the properties that make it suitable for nuclear applications. Subsequently, the limitations and challenges associated with current Zircaloy-based fuel cladding systems will be discussed, drawing insights from events such as the Fukushima Daiichi nuclear disaster and highlighting the vulnerabilities of this material under extreme conditions. Finally, the phenomenon of grid-to-rod fretting wear will be explained that can seriously damage the fuel claddings, elucidating the types of wear involved. To sum up, this section will discuss the importance of addressing degradation mechanisms for enhancing fuel cladding reliability and safety in nuclear reactors.

2.1.1 Nuclear plants: basic concepts

Over the last decades, nuclear power has been demonstrated to be an attractive option among the low-carbon energy resources. It produces more electricity density than any other known technique, does not use a relatively large land area and is independent of external variations, like the sunlight or wind²⁶. Nuclear energy is considered a low-carbon source because there is no generation of greenhouse gas during the energy production. Low emissions of gases are emitted over the full life cycle of the production, such as the uranium ore exploration and processing, fuel production, etc. However, the total amount of CO₂ generation during of the life cycle is very low in comparison to fossil fuel emissions²⁷.

In 2022, there was 437 reactors in operation worldwide and together they produced around 2600 TWh of electricity, which corresponds to approximately 10% of the total energy worldwide²⁸. Furthermore, the expectation is that the production of nuclear energy will increase as the world faces an energy crisis; energy demand

grows every year and renewable sources are urgently needed to overcome environmental issues²⁹.

Nuclear energy is the power provided from the atom core. The combination of two lighter atoms to form a heavier one is called a fusion reaction. While the splitting of a heavy atom into intermediate ones is known as a fission reaction. In both cases, the process to form stable atoms involves a loss of mass in the form of energy. In the nuclear power plants the energy is produced through a controlled fission reaction. In short, the atom splits and releases energy in the form of heat; this heat is used to create steam, the steam spins a turbine that generates electricity³⁰.

There is the possibility of the fission reaction occurring spontaneously with certain heavier atoms, such as 240 Pu₉₈ and 252 Cf₉₈. However, the probability of a fissionable atom undergoing fission is significantly greater if enough energy is provided to excite the nucleus. A strategy used is neutron-induced fission, where neutrons are absorbed into a fissile or fissionable nucleus. This interaction between the neutron and the nucleus makes the atom unstable, which then splinters into two nuclides. Beyond the new atoms and energy release, the product of the reaction also includes more neutrons and gamma radiation. The discharge of more neutrons can start a chain reaction inside the reactor. The main fuel used in the nuclear reactor is a fissile isotope of Uranium, 235 U₉₂³¹.

In general, the main components in a nuclear plant are fuel, cladding tube, moderator, control rod, coolant, reactor pressure vessel, steam generator and containment. The fuel is the fissionable nuclear material, which is most often UO₂ ceramic pellets. The cladding tube is designed to retain the fuel pellets and any radioactive products of the reaction. The moderator's main objective is to improve the fission by decreasing the speed of the accelerated neurons created in the reaction and reduce their mean free path. The control rods are used to control the fission reaction. The role of the coolant is to act as the heat-exchanger between the heat generated in the core and the steam generation. The steam generator is where the water evaporates to rotate the turbine and produce energy. And finally, the containment is an outer casing to protect and to avoid any leaking of the nuclear reaction products²⁶.

The most used reactors are the pressurized water reactors (PWR) and boiling water reactors (BWR). Both work in a similar way, water flows into the reactor core and becomes steam, the steam is conducted to turn the turbine-generator and finally produce electricity. After this process, the steam is condensed through a heat exchanger and returns to the same process. The main difference between PWR and BWR is how the steam is produced, as we can see in Figure 1. In the PWR, the coolant is kept liquid at high pressure in a primary circuit (about 15 MPa and 325°C) and exchanges heat with a second circuit, where the steam is created. On the other hand, in the BWR the steam used is directly from the coolant water that boils with the heat of the reactor, inside the core the water flows in an environment at around 7.5 MPa and 285°C^{26,32}.



A Pressurized Water Reactor (PWR)





PWR and BWR are classified as light water reactors (LWR), which means these reactors are moderated and cooled down using water (H₂O), as fuel they use enriched UO₂. As a contrast, there is a pressurized heavy water reactor (PHWR), where heavy water (D₂O) is used instead of H₂O, and natural UO₂ as a fuel^{26,32}. However, PWR's make up around 70% of all reactors in operation^{32,34}.

2.1.2 Zirconium alloys as fuel cladding

The fuel cladding is a key safety component in a nuclear power plant because it is the first barrier to protect the environment from the fuel and fission products. The fuel systems are uranium pellets piled inside 4 m long tubes made of zirconium alloys. Their outside diameter is around 10 mm, and the wall thickness can be from 0.6 to 0.8 mm. The rods are placed in spacer grids and organized in square sets of 10x10 for BWRs, and 14 x14 or 17x17 for PWRs (Figure 2). The fuel assemblies may consist of 800 tubes in a BWRs and between 150 to 200 in PWRs³.



Figure 2 - Schematic representation of a PWR fuel assembly showing the control rods, a fuel rod, and a fuel pellet³⁵.

Before the zirconium-based alloys, rods of stainless steel were used. However, throughout the years zirconium alloy manufacturing became cheaper, and they offer better properties in the nuclear core environment. The main advantage of Zr-alloys over steel is the lower absorption of thermal neutrons, which is beneficial for fission reaction efficiency since it allows more neutrons to be available inside the cladding. The zirconium itself has poor mechanical properties and low corrosion resistance, but the Zr-alloys show more interesting properties in the core of nuclear plants. The benefits of using zircaloys include acceptable mechanical properties like high hardness and ductility, which are relevant features to keep radioactive fuel inside the cladding. In addition, they provide higher corrosion resistance in a water environment of the reactor⁴.

The Zr-alloys were developed because zirconium itself has poor mechanical properties and low resistance to corrosion. However, even in the very beginning of zirconium-based alloys they still needed to be improved against corrosion, such as nodular corrosion, shadow corrosion from the waterside, and stress corrosion cracking from the fuel side. It was found that a low percentage of some alloying elements could minimize the problems with corrosion³⁶.

After that, the commercial alloys that have the best performance in nuclear reactors are mainly doped with niobium, tin, chromium and other elements, and the zirconium is at least 97% of the alloy composition. Generally, the established fuel rods alloys are Zircaloy-2, Zircaloy-4, M5 and Zirlo³⁷. Nominal compositions of some commercial cladding alloys are listed in Table 1.

Allov	Composition (in wt% or weight parts per million, wppm)						
7 110 y	Sn	Fe	Cr	Nb	Ni	0	С
Zircaloy-2 (ASTM B811)	1.2-1.7	0.07- 0.2	0.05- 0.15	-	0.03- 0.08	0.09-16	0.027 Max.
Zircaloy-4 (ASTM B811)	1.2-1.7	0.18- 0.24	0.07- 0.13	-	-	0.09-16	0.027 Max.
M5 [™] (Nominal)	-	150- 600 wppm	-	1	-	900- 1800 wppm	25-120 wppm
ZIRLO [™] (Nominal)	1	0.1	-	1	-	1250 wppm	
Optimized ZIRLO [™] (Nominal)	0.67	0.1	-	1	-	1250 wppm	

Table 1 - Cladding alloys compositions³⁷

In BWRs, zircaloy-2 is commonly used as a cladding, and in recent years the advanced version of zircaloy-2 with higher iron levels has been implemented. On
the other hand, zircaloy-4 was used as PWR cladding until the 90's, and they have been replaced with advanced PWR cladding alloys. Developments in PWR claddings were required to extend the cladding's life in more aggressive reactor environments, such as higher temperatures because of power uprates, higher pH to regulate the crud deposition on the fuel, and new additives introduced in the coolant for the reduction of cracking, etc. The advanced PWR claddings are ZIRLO[™], Optimized ZIRLO[™], and M5[™]. The difference from the zircaloy-4 is that these alloys have a reduction of tin and contain niobium. Consequently, they present a better performance in the reactor, for example, higher corrosion resistance and increased extracted energy from the nuclear fuel^{36–38}.

2.1.2.1 Fukushima Nuclear Accident

One of the main concerns of nuclear power are accidents, which although rare, cause massive damage to the environment and the public³⁹. The last major accident was in 2011 at the Fukushima Daiichi plant in Japan. The International Nuclear and Radiological Events Scale (INES) classifies this accident as level 7, which is the highest severity level. The Fukushima Daiichi disaster highlighted the vulnerabilities of current fuel designs under severe accident conditions, showing that improvements should be made to avoid the same problems and improve the reactor performance under severe conditions.

In the Fukushima accident, an earthquake caused a tsunami that struck the nuclear plant. To interrupt the nuclear chain reaction, neutron-absorbing control rods were introduced into the reactor core. Even though, heat generation continues from fission products and radioactive isotopes during radioactive decay. Therefore, an external source of power is necessary to circulate water and cool down the nuclear plant core. However, the tsunami flooded the generators and interrupted the power used in the reactor's cooling system. The company made many efforts to cool the reactor, but it was not enough, and the reactors overheated ².

One of the main problems in this accident was with the fuel cladding. Zirconium based alloys have been used for around six decades as fuel claddings in LWRs and under normal working conditions they have the expected performance and justify their long-term use⁴⁰. However, in the Fukushima disaster, the cladding tubes started to suffer physical and chemical degradation. Physical

damage appeared around 700°C and 1000°C, with problems such as ballooning and bursting. In addition, an oxidation reaction, that seriously aggravates the problem, occurred at high temperature between water steam and the fuel's Zr alloy cladding (Equation 1). The products of this exothermic reaction are zirconium dioxide and hydrogen – an explosive gas. Consequently, a terrible explosion occurred in the Fukushima nuclear plant and a considerable amount of radioactive material was released in the environment 2,5 .

$Zr + 2H_2O_{(g)} = ZrO_2 + 2H_{2(g)}$, $\Delta H = -584.5 kj/mol$ Equation 1

This disaster showed that a loss of cooling accident (LOCA) drastically changes the internal conditions of the reactor. This raised concerns about the structural integrity of the Zr alloys under these conditions that had previously shown acceptable performance for many years. After this disaster, the scientific community has been studying solutions to prevent this failure from recurring.

2.1.3 Wear on fuel cladding.

Wear phenomenon is a common problem faced in the normal operation of most machinery, including the nuclear plants. In this topic, the basic concepts about wear mechanisms and, in particular, the fretting wear problem on the fuel cladding will be discussed.

2.1.3.1 Wear mechanisms.

A definition of wear is the gradual removal or deformation of the surface of solid materials, resulting in damage over time. Tribology is the science that study the interaction between surfaces in relative motion, including the process of wear⁴¹. Wear in an industrial context causes high maintenance costs and concerns around the equipment safety. Due to that, understanding wear theory and mechanisms is essential to analyse and create solutions.

Most machinery components are made of metals and alloys. In general, the wear in metallic materials occurs through plastic deformation of the surface and by the release of fragments producing wear debris. However, the wear can propagate

in different ways: abrasive, adhesive, fatigue, fretting, erosive and corrosive/oxidation⁴². Figure 3 illustrated the main types of wear mechanisms.



Figure 3 – Wear mechanisms (a) Adhesive wear, (b) Two-body abrasive wear, (c) Three-body abrasive wear, (d) Fatigue wear, (e) Erosive wear and (f) Fretting wear⁴³.

• Abrasive wear: it occurs when a harder material removes material across a softer surface. This wear method could be explained when angular-shaped hard particles scratch the other surface. In other words, the load applied on one surface facilitates these particles to penetrate in the other material to a certain depth. As sliding occurs, the particles cut into the surface, creating depressions, and removing material as wear debris. Additionally, there are two mechanisms of abrasive wear, which are named two-body and three-body abrasive wear. The two-body method occurs when hard particles are simply removed on the opposite surface. While the three-body mechanism arise from hard particles detached and trapped between the surfaces, they are free to roll and slide⁴². Its

commonly identified by parallel groove lines in the surfaces, as shown in Figure 4.



Figure 4 - Example of abrasive wear in SEM identified in grooved parallel lines in the (a) vertical and (b) horizontal^{42,44}.

 Adhesive wear: it happens when materials are transferred from one surface to another in localized areas. Some forces may be responsible for making materials stick to each other, such as Van der Waals, electrostatic, frictional forces, and chemical bonding. Moreover, the adhered areas can create plastic deformation in the surface and produce surface particles known as wear debris. During this wear process, some modifications may occur, such as surface topography, loss of material, and likely mechanical failure. Figure 5 demonstrates the adhered rebar materials in a worn surface⁴².



Figure 5 - Examples of adhesive wear in SEM showing adhered rebar material in different samples: (a)⁴⁵ and (b)⁴².

• Fatigue wear: this type of wear is when the surface undergoes repeated stressing during sliding motion, creating cracks along the material structure after a particular number of cycles. Fatigue wear involves two identified mechanisms: the high-cycle fatigue and low-cycle fatigue. High-cycle fatigue occur after many cycles before failure, which increases the part life of the piece. In contrast, low-cycle fatigue involves only a few cycles to quick part failure. The successive cycles induce elasticity and the generation of wear particles. Additionally, in the first moment the wear debris are not generated, only plastic deformation in form of shallow grooves. After numerous cycles, the plastic deformation reaches a critical limit, and cracks are created. In general, crack propagation involves three stages: initiation, propagation, and post-critical stage, ultimately resulting in disastrous failure (as illustrated in Figure 6) ⁴².



Figure 6 - Examples of fatigue wear after the material frature⁴²

Fretting wear: it manifests when two surfaces have a periodic vibration in relative motion. This phenomenon usually occurs in unexpected locations. The displacement happens in a small amplitude of around hundreds of microns. Figure 7 shows how the fretting wear is recognized in the materials surface. The fretting wear usually develops because of a sequential event: Initially, the normal load creates a rough surface to adhere, then tangential oscillatory motion removes these asperities forming debris. Some remaining harder asperities can

interact with the smooth surfaces leading to plastic deformation, voids, and cracks propagation. Also, abrasion is created and extends laterally when there is a certain accumulation of debris in the surface depressions. As wear progresses in the form of adhesion, delamination and abrasion, debris spreads into surrounding areas. Additionally, elevated stress at the centre causes surface curvature and the formation of micropits, which merge into larger pits. Furthermore, depending on motion displacement, this process may lead to worm tracks or significant cracks on one or both surfaces^{41,42}.



Figure 7 - Examples of fretting wear appearance in the material surface⁴².

 Erosive wear: It happens when material from a solid surface is removed due to an interaction with a fluid containing particles, such as the impact of sand flow or vapour bubbles in locomotion towards the surface. As a result, craters are formed in worn surface as demonstrated in Figure 8. The wear degree is highly dependent on the materials properties and the environment conditions, such as the particles hardness and shape, and the fluid impact speed⁴².



Figure 8 – Examples of craters are formed during an erosion wear⁴⁶.

• Corrosive and oxidation wear: This kind of wear manifests by electrochemical reactions between the surface and a corroding medium. It could be either a wet environment, such as in water containing ions, or dry conditions, such as in the presence of some gases like nitrogen. The surface characteristics are shown in Figure 9. Usually, an oxide layer is created on the top of metallic surfaces, which reduces adhesive wear development because a metal-to-metal interaction can be more detrimental in wear aspects. Therefore, the oxide could be beneficial in reducing wear depending on the underlying material properties and the environmental conditions. For instance, when the metal has low hardness, and the load is relatively high, this metal will deform, and the oxide layer on the top may be destroyed. Then, the metal-to-metal interaction will manifest, leading to abrasion or adhesion wear susceptible to the mechanical and chemical properties of the material in contact. In this case, the oxide is not protective, and the wear rate is generally elevated. However, if the metal beneath is harder, it

can sustain the oxide film. Consequently, oxidation wear will not happen in this scenario^{41,42}.



Figure 9 - Examples of a surface after suffer corrosion wear⁴².

2.1.3.2 Fretting wear on fuel cladding

In the nuclear power plant, wear phenomena present a significant concern across various components and materials. The reasons for this are the combination of the harsh environment of the plants operating at 300 °C, 15 MPa pressurized water, strong surrounding irradiation (10²²n/cm²) and the fluid flow circulating through the components at high speed (4-6 m/s)⁴⁷. The fluid movement promotes vibration of the elements, which inescapably leads to wear, interface loosing and gaps^{7,48}. Tribological problems generate a high risk of damage and are the principal cause of failure of the components. For instance, the flow-induced vibration (FIV) commonly leads to replacement and repair of the steam generators, because the heat exchange process induces an oscillatory movement between the tubes, resulting in fretting⁷.

The FIV is also present in a more concerning component: the fuel cladding. In the nuclear core, the fuel claddings are held in a spacer grid assembly. The grid material is usually Inconel (nickel-chromium-based alloy) or Zircaloys²⁶. Then, the coolant flows through the fuel rods and induces a vibration at the grid-to-rod interface (Figure 10). This repeated movement is known as grid-to-rod fretting (GTRF) and over long time periods causes a gradual relaxation of the grid, increasing the gap between the cladding and the grid. As a result, there is a significant increase of fretting motion between the surfaces, which leads to fatigue problems, stress corrosion cracking and wear damage ^{7–11}.



Figure 10 - Example of PWR fuel assembly⁴⁹

A schematic illustration of how the grid-to-rod fretting happen is shown in Figure 11 (a) and (b) an example of serious wear scars on the fuel rods surface caused by this phenomenon.



Figure 11 – (a) Schematic illustration of grid-to-rod fretting problem⁵⁰ and (b) severe wear scars in fuel claddings ⁵¹.

In the 60's, the GTRF was identified as the origin of fuel rod failures, and since then many efforts and improvements have been made to solve this issue. However, as reported in some review papers about fretting wear in nuclear plants, GTRF is the main cause for the fuel rod failures in PWRs ^{7,47,52–54}. For instance,

Kim *et al.* studies showed the primary causes of fuel tube failure to be grid-to-rod fretting, excessive cladding corrosion, and fuel assembly bowing. Among all the listed failure reasons, they reported that the GTRF phenomenon was the leading cause of fuel rod failures⁶. Additionally, as presented in Figure 12, almost 90% of fuel failures were caused by GTRF between 1999 and 2002. Over the years, although improvements were implemented and this proportion dropped, the GTRF still caused about 60% of the problem in the last reports⁴⁷.



Figure 12 – Percentage of the main causes of fuel failure in the world⁴⁷.

The failure of cladding rods is the most relevant issue in the daily operations of cladding in LWRs. The main concern in the fuel cladding is that damage may lead to leaks, where the radioactive fission gases from the fuel could escape to the coolant and increase the radioactivity in the nuclear plant. While a complete perforation may not happen, the strength of the fuel claddings would be reduced due to a thickness reduction created by wear ⁴⁷. Fuel failure also has a significant economic impact on the plants once it requires replacement often to avoid fuel leaks⁵⁴.

As with most engineering challenges, singular solutions are rarely the optimal path forward. Therefore, extensive studies have been done to find viable solutions around mitigating GTRF occurrence. The approaches involve enhancing the design of coolant flow channels to diminish the force inducing rod vibration, enlarging the contact between the grid and rod to create better support conditions, strengthening the rod restraint at the base of the fuel assembly to minimize rod vibration, and advanced materials for cladding and grid construction to improve resistance against fretting wear⁵².

Regarding the progress of advanced materials, after the Fukushima nuclear accident, the development of accident-tolerant fuel (ATF) has been intensively discussed. Additionally, the impact of an ATF could be highly beneficial to the GTRF problem. Some previous studies have shown that coated Zr-based cladding was effective in reducing the damage in fretting wear experiments^{8,55–57}. Some of these studies will be discussed deeply in the next section (2.2.3).

However, the complexity of this system and the problem demand more studies and tests around the development of advanced materials applications. It is important to acknowledge the challenges and economic constraints associated with simulating the harsh conditions of a nuclear reactor's real environment. Typically, experiments are conducted under dry, non-flowing, room temperature, and atmospheric conditions⁵².

2.2 Development of an Accident-Tolerant Fuel (ATF)

Acknowledging the crucial role of fuel claddings and the current challenges faced by nuclear power plants, there is an urgent need to develop an accident-tolerant fuel (ATF) to enhance safety within the LWR core. ATF is mainly designed to extend the coping time in an accident scenario, reduce the hydrogen source production and avoid high-temperature oxidation. However, the ideal cladding should also enhance its performance under normal operating conditions, such as reducing the GTRF phenomenon. The results of advanced nuclear fuel cladding systems could extend its lifespan and drive economic advancements in nuclear power ¹².

The most promising route to create an optimum advanced nuclear fuel cladding system involves the study of advanced materials and understanding their behaviour under the plants environments and conditions. Therefore, investigations should focus on materials that are able to maintain or to improve the safety of the existing Zr alloys, as well as be compatible with the nuclear fuel and reactor systems in existing plants^{13,14}.

The industry requirements for an acceptable material in a nuclear reactor is extensive, it mainly involves three areas: economics, accident performance and materials performance. On the financial side, a new fuel design should be assessed for its the cost and benefit in terms of longer cycle lengths, higher fuel burnups, and manufacturability, for example. The accident performance focuses on identifying safety concerns within a reactor that could impact cladding and fuel integrity, enabling engineers to develop and implement strategies to mitigate potential issues in nuclear plants. For instance, there is a list of the Design Basis Accidents (DBA) that involves problems such as the Loss of Coolant Accident (LOCA). Also, there is the Beyond Design Basis Accident (BDBA) list that are postulated to prevent consequences such as cladding resilience to chemical reactions during accident conditions^{5,14}.

Regarding the materials properties, there are several requirements to be an acceptable candidate and be applied as fuel cladding. These include the chemical compatibility of the fuel and cladding with other components within the LWR core, their respective melting temperatures, thermal conductivity, thermal neutron cross-section, manufacturability, gas retention capabilities, and radiation performance. Furthermore, a lower interaction with oxygen at high temperatures is desirable with minimal hydrogen production, higher capacity to retain and protect the fission elements, enhanced mechanical properties at higher temperatures, no chemical reactivity with other LWR components and good manufacturability¹⁴.

Recent studies have considered two main prospective cladding solutions to address these objectives. Firstly, exploring an alternative material to entirely supplant the existing Zr alloy cladding. Alternatively, coating the exterior surface of the Zr alloy cladding with a thin layer of a different material presents an alternative strategy to provide enhanced protection. In the following topics both strategies will be discussed, showing the most used materials and recent findings in each option.

However, before presenting both strategies, an important topic for designing an ATF will be briefly introduced: the critical heat flux.

2.2.1 Surface properties and critical heat flux (CHF)

The comprehension of heat transference in the core of the nuclear reactor is crucial when considering a new ATF technology. The heat transfer process involving the liquid-vapor phase change is determined by a "curve" defining the functional correlation between the heat flux of the surface and its temperature. Figure 13 presents an illustrative curve of this kind, showing the relationship between the heat flux on the heater surface (q") and the degree of superheating on the heater surface (Tw-Tsat), where Tw is the surface temperature and Tsat is the saturation temperature corresponding to the pressure of the flow system ⁵⁸.



Figure 13 - Typical boiling curve showing the variation in heat flux (q") as function of surface temperature $(T_W - T_{sat})$, highlighting critical points: Onset of nucleate boiling (A), critical heat flux (B), leidenfrost point (C), and film boiling (D).

The external heat source is transferred through the surface to the liquid in contact with the cladding. Then, the boiling process follows the route A>B>D. The boiling process is usually maintained below point B to ensure the safety of the nuclear power plant once it prevents a significant temperature rise. Conversely, the quenching process – the rapid cooling of a component using a coolant fluid – pursues the route D>C>B>A. During the boiling process, the heat is transferred to

the liquid and vapour bubbles are created. These bubbles will enlarge with the temperature increase to the point where a constant vapour film is produced on the surface of the fuel cladding. At this point, the critical heat flux (CHF) is reached, which is characterized by an intense evaporation of liquid attached to the heated surface. The issue of achieving CHF in both the boiling and quenching processes is that the heat is used for the phase transition instead of heat transfer. Consequently, the temperature rises drastically, leading to surface overheating, which may damage the material ^{58,59}.

Understanding the CHF phenomenon is essential to designing an ATF and guaranteeing reactor safety, where a new material should improve and not decrease the CHF limit. For many years, CHF was considered a hydrodynamic phenomenon, however, surface characteristics are crucial and can exert an influence. Surface roughness, wettability, porosity, and the thickness of the oxide layer on the surface are among the critical surface parameters known to impact CHF⁶⁰.

For instance, the literature acknowledges the influence of contact angle on CHF. Generally, CHF increases as the contact angle decreases. This behaviour is because the smaller the contact angle, the greater the wettability or the more hydrophilic the surface. Consequently, the bubble departure frequency from the surface is reduced, and the CHF is increased⁵⁸. It was reported that the optimum heat transfer coefficients were obtained on surfaces with contact angles between 0° and 90° ⁶¹.

Therefore, once recent research indicates that some aspects of the surface seem to affect CHF, it is crucial to investigate changes in surface characteristics in an ATF.

2.2.2 Alternative materials to Zr-based alloys

Some claim that the main disadvantage of coatings is the possibility of delamination during an accident, exposing the Zr-based alloys to a corrosive environment¹³. Due to that, some investigations focus on the alternative approach of a substitute material. The new candidate should maintain the same performance quality as the current claddings and provide benefits during accidents and normal operation conditions.

On the other hand, introducing a different material in a stable and harsh environment is complex. Before an actual application, several assessments of the material properties and performance in the nuclear core should be considered. The main features to be a material be contemplated as an option are: neutron absorption, feasible manufacturing, corrosion and radiation resistance, thermal and mechanical properties. Some materials are commonly mentioned in the literature as a possible option, such as silicon carbide (SiC), FeCrAl alloy, MAX phases, and Mo alloys^{5,12–14}.

2.2.2.1 Silicon carbide

SiC-based cladding is a promising candidate for LWR core conditions, the benefits of this material include higher melting point, reduced hydrogen formation under accident conditions, and lower neutron absorption cross-section⁶². To illustrate, in comparison with the existing Zr claddings, the SiC presents 25% less neutron absorption and reacts at a slower rate with steam¹².

SiC-based cladding holds the potential to offer increased safety margins and enables high burnup capability, which allows for longer cycle lengths or uprated operation because it accommodates higher heat fluxes. Furthermore, studies presenting chemical compatibility tests between fuel and cladding suggest minimal interaction between silicon carbide (SiC) and uranium dioxide (UO₂) at temperatures below 1200°C in a no irradiation environment ^{63,64}.

As expected in a ceramic material, monolithic SiC tends to experience brittle failure when subjected to sudden mechanical impact. The damage makes the component unusable and creates foreign debris, increasing the risk of fuel failures during operation. A viable option to reduce the brittleness is utilizing a SiC fiber-reinforced and SiC matrix (SiCf/SiCm) structural composite, which boasts more desirable properties, including superior thermal, mechanical, and chemical stability. In more detail, the cladding is structured in a layer-pair configuration, consisting of an outer layer made of SiC ceramic matrix composite (CMC) for enhanced strength and an inner layer made of dense monolithic β -SiC for gas impermeability¹³. However, because of the more complex structure, the thermal conductivity is reduced. In addition, the SiC/SiC composite is thicker than usual, requiring fuel enrichment to compensate the volume lost¹⁴.

Although this material has been studied for more than 50 years and claimed as the most impressive ATF option beyond an accident condition, it still has several challenges to an actual application⁶⁵. For instance, the thermal conductivity of SiC is seriously affected by temperature and irradiation, rendering it a crucial aspect to evaluate when incorporating SiC cladding tubes. Also, the fabrication of thin-walled and long rods of a ceramic material is more complex than a metal tube ¹², which could make the production process about 30 times more expensive than the Zralloy cladding ¹⁴. Furthermore, there are concerns around managing the effects of fission products, corrosion under normal operating conditions in PWRs, and ensuring the hermetic sealing of end caps¹³.

Other variation and combinations using SiC layers has been under investigation over the years to overcome this material limitation. A tested design known as "triplex" incorporates both monolithic SiC layers on the inner and outer sides, with a middle layer composed of SiC fiber-wound composite. The results showed that the SiC specimens presented a low irradiation-enhanced corrosion rate and consistent swelling patterns. However, because of the SiC lower thermal conductivity, the fuel will undergo elevated temperatures⁶⁶. Another example is the Brachet *et al.* investigation on a "sandwich" cladding design with SiC/SiC layers and a metal liner between them, shown in Figure 14 .The authors demonstrated that this composite had low sensitivity under steam oxidation environment and irrelevant mechanical properties damage at 1200°C. Although the first results seem suitable, the authors state that several tests must be done to consolidate the use of SiC and this concept of a SiC "sandwich", such as more investigations around irradiation⁶⁷.



Figure 14 – Sandwich cladding design with SiC/SiC layers and a metal layer in the middle.

2.2.2.2 Fe-based alloys (FeCrAl)

Fe-based alloys have the potential to be cladding materials due to their good formability, excellent thermal conductivity, high strength, and excellent oxidation resistance at high temperatures. Ferritic alloys containing Cr and Al, like Iron-chromium-aluminium (FeCrAl) alloy, is often mentioned as an excellent candidate once they produce an oxidative protective layer (Cr₂O₃ and Al₂O₃) at high temperatures and in steam environments^{68,69}. This alloy is usually employed within industrial proposes in high temperature and oxidative environment, and it has been considered for the nuclear industry for the last 50 years⁷⁰.

To illustrate, when tested in the normal and off-normal operation condition of a LWR, the FeCrAl alloy presented superior oxidation resistance at 1200°C in steam and at 360°C in pressured water than Zr-alloys⁷¹. In addition, iron alloys showed improved mechanical properties, such as an acceptable yield strength and creep rupture strength at high temperatures in unirradiated tests⁶⁹.

Studies regarding fretting wear on FeCrAl fuel cladding examined the coefficient of friction (COF), which serves as a method to evaluate the wear resistance of a material across varying temperatures. The findings showed that these alloys outperformed Zircalloy-4 in terms of wear resistance because they develop a protective layer (consisting of alumina and chromia) that enhances their wear behaviour in PWR dry fretting tests^{9,72}.

Although researchers can explore changes in the composition of the alloy elements or add new alloying elements to improve the performance of iron alloys, certain challenges remain once it is intrinsic to the material⁵. For instance, a crucial concern is the higher neutron absorption cross-sections on FeCrAl related to Fe and Cr. Iron alloys account for 4 to 6% of neutrons absorbed in the cladding compared to around 1% in the Zr-based cladding. Moreover, the PWR generate a considerable amount of tritium from the dissolved boric acid in the coolant. It has been reported that the ferritic alloys permit approximately two orders of magnitude more tritium permeability compared to zirconium alloys⁷³. Understanding the implications of this disparity is essential before contemplating the use of iron alloys.

In addition, the system fuel and FeCrAl cladding under severe accident conditions underwent extensive studies, with promising results in slower oxidation kinetics, less H₂ production, and increasing coping time^{74,75}. However, a concerning result shows corrosion appearing close to 1500°C. These findings affirm the necessity for additional studies to fully understand this cladding material's performance under conditions beyond DBA⁷⁶.

2.2.2.3 MAX phases

Max phases refer to layered, hexagonal carbides and nitrides characterized by the generic formula M_{n+1}AX_n. In this formula, M represents an early transition metal, A is an A-group element (primarily from groups IIIA and IVA, or groups 13 and 14), and X represents either carbon, nitrogen, or a combination of both ⁷⁷. MAX phases were first discovered in the 60s, but most of the 150 distinct combinations of elements have only been synthesized recently⁷⁸. The great advantage of the MAX phase is that they combine both the properties of metals and ceramics, like thermal conductivity and high temperature strength, respectively. Overall, the merger properties of the MAX phases make them a potential option for nuclear fuel cladding in ATF for PWRs. Particularly, some MAX phases have shown properties like radiation resistance, and anti-corrosion and anti-oxidation in contact with the coolant ^{77,78}

Ti₃SiC₂ is an example that presents attractive properties to use as nuclear cladding⁷⁹. Research into this material has demonstrated excellent thermal conductivity, even higher than the traditional Zr cladding under normal operating

conditions. In addition, Ti₃SiC₂ demonstrates a high melting point – over 1700 °C – and good tensile properties from room temperature until 1100 °C. However, Ti₃SiC₂ also presented some limitations that raised doubts about its application in nuclear equipment. For instance, regarding oxidation tests, the Ti₃SiC₂ oxidization resistance is drastically reduced after 700 °C, and there is no information on how this material reacts in a high-temperature steam environment⁸⁰. Moreover, there is evidence that Ti₃SiC₂ presented diffusion problems with fission products at elevated temperatures⁸¹.

As a second example, Zr₂AlC has also been suggested as a possible option on the nuclear core because of its properties and it is Zr-based^{82,83}. The advantages of this material include its excellent neutron transparency and potential resistance to irradiation. In addition, the aluminium present in the composition creates on oxide layer that protects against oxidation in high-temperature steam⁷⁷. Nevertheless, although the literature speculates that Zr₂AlC could be a potential substitution for Zr claddings, investigations into Zr₂AlC behaviour must be conducted in high-temperature steam to confirm this material's effectiveness in nuclear-plant conditions.

2.2.3 Protective coatings for Zr-alloys claddings

Coating is one of the most promising routes for a near-term solution, as it does not modify the existing zirconium-based rods, making it more economical and quickly commercialized (between 5 and 10 years). In addition, some previous studies demonstrate significant results for the coated Zr alloys, such as higher melting point, improvements in corrosion and wear resistance, and lower hydrogen generation at elevated temperature¹³.

The material deposited onto the fuel cladding should provide improvements to the cladding system, such as a lower oxidation rate than Zr alloys, lower neutron absorption cross section, higher melting point, low hydrogen generation, sufficient strength at high temperature, increased thermal conductivity, minimal differences to the mechanical properties with Zr alloy cladding and chemical compatibility with other LWR components. It also essential that the coating has a similar coefficient of thermal expansion (CTE) and melting point to the substrate¹⁴.

In addition, the coating must be dense, adhere well and remain chemically stable with the Zr-based cladding substrate under normal and abnormal conditions. Moreover, it should mitigate the risk of grid-to-rod fretting failure⁵. Furthermore, to be a practical solution, the coating process must be suitable for scale up to 4 meter full length fuel rods and exhibit manufacturability at a reasonable cost¹⁴.

The coating could be metallic, ceramic or composites. Metals usually present excellent thermal conductivity and oxidation resistance when forming a protective oxide layer that reduces O₂ diffusion and oxidation rate. Meanwhile, ceramic coatings can increase substantially the hardness of the claddings. On the other hand, a combination of metals and ceramics can be obtained in a composite material, and the cladding fuel system could be enhanced with corrosion resistance and hardness. However, each class of material has its pros and cons, and each case should be studied in the nuclear core environment¹².

Various materials have been explored for coating Zr alloy cladding in the pursuit of an appropriate coating. Studies show that the most suitable ATF coating technology should incorporate at least one of the elements: Cr, AI, and Si^{5,84}. Due to their ability to form chromia (Cr₂O₃), alumina (Al₂O₃), or silica (SiO₂), which exhibit high-temperature steam oxidation resistance^{85–87}.

Coatings designed to generate alumina or silica have mainly appeared as MAX-phase compounds. In most studies, chromium is primarily considered in the metallic form, but it is also considered as ceramic in chromium nitride (Cr_xN). In a different perspective from the oxide-forming films, TiN has also been investigated as a coating material⁵.

2.2.3.1 Al-based coatings

Promising results for nuclear applications were reported using Ti₂AIC MAX phase as a coating onto Zr-based cladding ^{88–91}. Maier *et al.* performed mechanical and oxidation tests on Ti₂AIC coatings on Zr-4 substrates coated using cold spray technology. The results demonstrated high density and well-adhered coatings after the scratch test, higher hardness and wear resistance than the substrate, and effective protection to the substrate was noted at elevated temperatures⁹¹.

Another study was conducted to investigate the behaviour during irradiation tests of Ti₂AIC films deposited on Zircaloy-4. The samples were annealed after

being deposited, which formed Al-rich intermetallic phases. The authors reported that after the irradiation test, most of these phases suffered amorphization, and the coating and the intermetallic phases became harder than Zircaloy-4. Therefore, a realistic consideration of Ti₂AIC as a cladding coating still needs systematic investigations of the irradiation-induced changes in the structures, such as the thermal, mechanical, and chemical stability in reactor environments⁸⁹.

2.2.3.2 Si-based coatings

Some studies about zirconium-silicide – ZrSi, Zr₂Si or ZrSi₂ – oxidation resistance in high temperatures indicate that this ceramic could be a candidate for a coating on fuel claddings^{92,93}. Three stoichiometric forms of zirconium-silicide coating on Zircaloy-4 using magnetron sputtering were conducted to test their performance. An air-oxidation test at 700°C for 5h demonstrated that ZrSi₂ had the best oxidation resistance because it was dense and due to the formation of a silica protection layer. Also, the pre-oxidation of ZrSi₂ showed an improvement in the oxygen diffusion in air-oxidation analysis at 1000°C and 1200°C for 10 min. Moreover, there was no spallation or cracking in the ZrSi₂ coating during air cooling to room temperature after high-temperature oxidation tests⁹⁴.

Water quenching tests were also conducted on ZrSi₂ deposited on Zircaloy-4 via magnetron sputtering. The results showed enhanced quenching heat transfer on the coating surface. It was reported that the minimum film boiling temperature was raised by around 6-8%, which is modest but still positively impacts the heat transfer of the cladding. In addition, the coating did not present any surface degradation after three aggressive thermal cycles of water quenching between 700°C and 850°C in 20s⁹⁵. Although ZrSi₂ seems to be a good coating material, more investigations around mechanical testing are needed, such as wear resistance, scratch test, and hardness measurements.

2.2.3.3 Chromium coatings

The most promising and extensively researched coating technologies for Zrbased alloys thus far are those based on chromium, specifically chromium pure metal and Cr_xN⁵. Chromium is a body-centred cubic (BCC) structured, brittle

transition metal with a steely-grey colour and a shiny appearance. It is of high interest to the industry due to the high hardness, high melting point and good corrosion resistance.

Compared with other coatings the advantages of using Cr, such as:

- Cr has high and similar melting point to that of Zr, around 1907 °C and 1855 °C, respectively.
- Cr has a similar coefficient of thermal expansion (CTE) to Zr, 6.5 × 10-6/K and 5.77–7.62 × 10-6/K, respectively¹⁵. This characteristic can avoid cracks and deformations in case of a mechanical deformation in the coating-cladding system, which can expose the substrate to the environment in accident conditions.
- Cr demonstrates a relatively lower thermal neutron absorption crosssection (Cr =2.9 barn) when compared with other coating materials¹⁵.
- Cr has about double the elastic modulus of Zr, which is beneficial for enhancing the stiffness of the cladding system¹⁶.
- Cr forms a passive oxide film (Cr₂O₃) at high temperatures and oxidative environments (similarly to LOCA conditions), which is stable at high temperatures, aqueous and steam environments^{17,96}.
- Excellent oxidation resistance in normal and LOCA conditions and beyond^{97,98}.
- Good adhesion to the coating matrix¹⁸.

For these reasons, Cr coatings have a high probability of maturing into an industrial material with substantial potential¹².

The oxidation performance under accident conditions is the main improvement expected when designing an ATF. However, the behaviour in normal operating conditions should not be changed or may be enhanced. Some investigations were conducted to understand the chromium coated Zr cladding behaviour under normal conditions in the nuclear plant and showed positive results. One study in specific, created a similar environment of a nuclear plant, the oxidation tests were mostly conducted in 360 °C and 18.6 MPa pressurized water ¹⁵. After the experiments, the findings demonstrated the formation of Cr₂O₃, and no cracks or delamination were observed. Moreover, it was reported that the weight

gain of the Cr-coated samples was significantly lower in comparison with only uncoated Zr alloys.

In another study, Brachet *et al.* carried out an autoclave oxidation test at 415°C, steam, and pressurized environment (10 MPa) for 200 days. They compared the bare Zircalloy-4 and Cr-coated using a physical vapour deposition (PVD) technique. The Cr coating tests included different thicknesses and densities. They reported that there was a significant oxidation reduction when using Cr-coatings. Moreover, a weight gain of 50 times less can be observed in the denser coatings compared to uncoated reference materials. They concluded that a fully dense Cr-coating exhibits promising behaviour under the reactor's nominal conditions⁹⁹. Similar results were reported by Liu *et at.*, with Cr coated Zirlo by magnetron sputtering. It was shown that the weight loss was reduced by 50% after 45 days of autoclave testing (315°C and 16.6MPa) compared to the substrate only¹⁰⁰.

On the other hand, tests assessing the oxidation resistance of Cr-coated Zr alloys are essential to evaluate the quality of this technology. During a Design Basis Accidents (DBA) scenario, the temperature of a nuclear plant core can reach 1200°C. A few studies have been done to understand the oxidation in LOCA conditions of chromium as a coating in Zr-alloys. The investigations have demonstrated that chromium coatings significantly reduce the high temperature steam oxidation kinetics^{98,101–104}.

Kashkarov *et al.* conducted an interesting investigation about steam oxidation experiments from 500 to 1200°C on Cr-coated Zr alloy using magnetron sputtering. They assessed the microstructure and thickness of the coatings, and due to that, three types of coatings were prepared: one fully dense Cr coating of 4.5 μ m (Cr-4.5) and two columnar coatings of 6 (Cr-6) and 9 μ m (Cr-9). The mass gain results as a function of temperature for these three samples and the Zr alloy (Zr-4) are shown in Figure 15¹⁰⁵.



Figure 15 – Zirconium alloys with Cr-coated and uncoated surfaces mass gain during transient tests at 500-1200°C in steam flow¹⁰⁵.

As can be observed, the steam-oxidation resistance of zirconium alloy is improved by chromium coatings during the temperature increase. While the mass gain of the Zr alloy is 11.38 mg/cm² at 1200 °C, Cr-4.5 presented 5.03 mg/cm² at the same temperature. On the other hand, Cr-6 and Cr-9 had a total mass gain of 2.88 and 1.73 mg/cm², respectively. Also, it can be noticed that Cr-4.5 had the lowest mass gain rate until 1120 °C. Around 1100 and 1120°C, there was a transition point where the oxidation kinetics were drastically increased. Then, the Cr-4.5 presented the worst performance, and the Cr-9 demonstrated the best protection at 1200 °C for 10 min¹⁰⁵. Demonstrating that thickness plays an important role in resistance to oxidation.

Maier *et al.* studied Cr-coatings onto Zr alloys deposited by cold spray technology and the results were also encouraging. The oxidation tests in air at 1300 °C for 20 min showed that the Cr-coating layer was intact and had excellent oxidation resistance. It also presented an effective chromium oxide protection layer for the rods with around 12-24 μ m thickness¹⁷.

A consequence of the high temperature and oxidation environment is the consumption of the chromium coating for the Cr₂O₃ formation and diffusion through

to the zirconium substrate, forming a ZrCr₂ layer. It was reported that the dissolution of chromium atoms into Zr weakens the substrate's strength¹⁰⁶. Additionally, the Cr-Zr eutectic temperature is 1332 °C, which is above the design basis accident temperature (1200°C), but it can cause rapid failure of the coating beyond DBA conditions. The eutectic point is the lowest melting temperature possible that a mixture of substances can reach. A possible solution is to create an interlayer with a different material to avoid the diffusion between Cr and Zr. Also, this interlayer should have a higher eutectic temperature, then the diffusion between the material does not cause damage to the structure in high temperatures. Some studies are being done using an interlayer of molybdenum (Mo), CrN, and $ZrO_2^{106-108}$.

A Cr coating on a Zr alloy surface can also influence the mechanical properties of a cladding tube, which are exhibited by its adhesion properties, burst resistance, and hardness tendency. During accident conditions, the cladding can suffer extreme deformation due to a possible thermal expansion, irradiation-induced growth, and ballooning, resulting in the coating substrate's detachment. Due to that, the adhesion of the surface coatings is essential when considering a coating. The adhesion and strength of a Cr coating on Zr were investigated using scratch, ring tensile, and compression tests^{18,109–111}.

Kim *et al.* coated Zircaloy-4 with chromium using a 3D laser and tested the adhesion with ring compression and tensile tests. They claim that the tensile and compressive strength is slightly improved compared to the bare substrate. In addition, no coating spallation or peeling was found after the test¹⁸. Huang *et al.* used the scratch test to compare the adhesion of Cr and Al coatings via magnetron sputtering on Zr-4 alloy. Their findings showed the superior adhesion of chromium once its critical load was more than 100 N, while for the Al coating it was 20N¹¹².

Ballooning and rupture of the cladding tubes can happen under increasing temperatures and pressure in the reactor core. Some studies reported an enhanced burst resistance in the presence of Cr coatings ^{18,113,114}. According to a recent study published by Hazan *et al.*, semi-integral LOCA tests were conducted on cold-sprayed Cr-coated Zr alloys and bare Zr alloys. The results demonstrate that the Cr-coated samples suffer a burst after 30 min, while the uncoated samples rupture in less than 6 min. In addition, the circumference maximal deformation was 14.5% for Cr-coated and 178% for the bare substrate¹¹⁴.

Park *et al.* also showed similar results by using cold spray to coat Zr alloy tubes. They reported a higher temperature of burst for the Cr-coated cladding. Additionally, the burst damage is visibly smaller, as can be seen in Figure 16. The authors reveal that despite minor cracks on the surface around the ballooned area, no significant cracking or spallation was found in the Cr coating after the integral LOCA assessment. They claim that the abrupt change in the temperature during LOCA tests had little influence on the adhesion between the coating and the substrate¹¹³.



Figure 16 – Photos of the ballooned area and burst of Zr cladding tubes (a) Cr coated and (b) uncoated after integral LOCA experiment¹¹³.

Several investigations showed that the cladding hardness can be increased when coated with chromium, significantly improving the wear resistance in GTRF tests. Reed *et al.*, for example, obtained a hardness of 3.8 ± 0.5 GPa for Cr-coated ZIRLOTM using cold spray, contrasting to 2.6 ± 0.3 GPa of the uncoated ZIRLOTM. Leading to an 80-90% improvement of the wear resistance⁸. Similarly, Liang *et al.* produced three chromium coatings via electrodeposition with different parameters onto stainless steel samples. They reported microhardness values between 790 Hv and 910 Hv using a Vickers test and 100g load, and near zero wear in all coatings was observed, either during long or short-term wear tests¹¹⁵.

A recent investigation by C. Wang *et al.* studied the wear behaviour of hard chromium coatings under influence of the friction velocity¹¹⁶. The coating was

deposited on 45# steel substrate by electrodeposition. The Cr-coated samples demonstrated a hardness of around 14 GPa. The friction test was carried out under 5N normal load, and the frequencies used were: 6, 10, 15, 20, 25 and 30 Hz. The wear rates and wear tracks are shown in Figure 17.



Figure 17 – (a) Wear rates and (b)3D morphologies of wear tracks of chromium coating under varied friction frequencies²⁵.

As can be noticed in Figure 17, although quite similar, the highest wear rates were observed at 10 Hz and 15Hz, with 9.84 and 9.19 x10-4 mm³/N.m. The authors related the downtrend from 10 to 30 Hz to the moderate thickening and increased toughness of the frictional oxide film, because as the frequency increases the temperate elevated at the interface. The authors concluded that the wear pattern on chromium is a result of three mechanisms: oxidation wear, abrasive wear, and plastic deformation. The combination of these mechanisms resulted in a relatively slow wear rates across a broad spectrum of frictions frequencies.

2.2.3.4 Cr_xN

The literature also reports chromium nitride (CrN) as a competitive candidate for coating onto Zr alloys. As a ceramic material, Cr_xN is brittle, exhibits high hardness, and excellent thermal properties and oxidation resistance^{19,20}.

Chromium nitride primarily forms two crystalline structures, determined by the nitrogen content during deposition. Nitrogen-rich films will form cubic-structured CrN, while nitrogen-poor films will form a mixed phase or hexagonal-structured Cr₂N. Even when the coating's stoichiometry is ideal for CrN (with mass percentages of 79% Cr and 21% N), some Cr₂N is likely to be present¹¹⁷.

Many studies have tested CrN as a coating in zirconium claddings. For example, Meng *et al.* deposited 13 μ m uniform CrN coatings on Zr alloy substrates using multi-arc ion plating technology. Then, they studied the oxidation resistance at high temperatures of the coated and uncoated Zr substrates. The results of this study are presented in Figure 18, which shows photographs of the samples before and after the oxidation tests in air from 760 to 1160 °C.



Figure 18 – Photographs of uncoated Zr alloys (a) and CrN (g) before oxidation and after oxidation at (b) (h) 760 °C, (c) (i) 860 °C, (d) (j) 960 °C, (e) (k) 1060 °C, and (f) (l) 1160 °C²⁰

As shown in Figure 18, the CrN coating shows no signs of cracks or spallation after the air oxidation test at high temperatures. Conversely, on the uncoated Zr alloys at 860 °C, irregularly distributed cracks and a black oxide film are noticed on

the surface. Then, as the temperature increases, the samples' appearance worsens: the black oxide film detaches from the surface, and more wrinkles and cracks are observed. Moreover, the weight gain increased by almost 98% after the oxidation test at 1160 °C, accounting for 85.66 mg/cm² for the Zr alloy and 1.97 mg/cm² for the CrN-coated Zr. In addition, they reported that the CrN film improved the hardness of the coated substrate. The uncoated Zr showed a hardness of 3GPa, while the CrN-coated Zr alloys presented better hardness than bare zirconium (9 GPa)²⁰.

A study conducted by Krejčí *et al.* compared pure Cr, CrN, sub-stochiometric CrN (Cr 90 wt% and N 10 wt%), and two types of multi-layer CrN +Cr (one thin coating with 3.2 μ m and a thick coating of 12.8 μ m). The deposition technology chosen was unbalanced magnetron sputtering and reactive magnetron sputtering. The samples were submitted to mechanical and high-temperature steam oxidation tests from 1000 to 1400 °C, simulating a LOCA accident and a design extension condition. In general, all the coatings indicated a protective action after the experiment. However, each coating variation showed pros and cons.

First, the metallic Cr-coated sample demonstrated excellent corrosion resistance, ductility, post-quench ductility and preserved integrity. However, the pure Cr diffused into the Zr substrate, melting the interlayer due to the Cr-Zr eutectic temperature. Second, the CrN coatings showed a decomposition at temperatures between 500 and 975 °C, which caused cracks in the coating and poor ductility related to the ceramic material. Nevertheless, CrN presented exciting inter-diffusion results because it released N₂ at high temperatures, creating a thin stable ZrN layer that inhibits Cr-Zr diffusion. Third, the thick CrN+Cr coating demonstrates a promising combination with enhanced oxidation resistance, improved mechanical properties, and restrained the Cr-Zr eutectic formation¹¹⁸.

Tricoteaux *et al.* examined the fretting wear behaviour of CrN and Cr₂N coatings. The ceramic films of 1.5 μ m thickness were deposited on 50CrMo4 steel substrates using reactive magnetron sputtering as the deposition technique. The fretting wear tests were conducted under a high load (97 N) in dry and grease lubricant conditions. They reported that in a dry environment, the CrN and Cr₂N coatings were quickly damaged, producing hard debris that acted as abrasive

particles and elevated the wear rate. However, there was a significant enhancement when the lubrication was used¹¹⁹.

More promising results on wear resistance were shown when CrN was combined in layers with other materials^{56,120}. For example, Guan *et al.* conducted an interesting study on the tribological properties of multilayer systems. They tested four different metal/ceramic combinations: Cr/CrN, Cr/ZrN, Zr/CrN and Zr/ZrN. The coatings were deposited by interspersing a metallic layer and a ceramic layer until 15 layers were completed in total, as can be seen in Figure 19. They used a multi-arc ion plating system to deposit the films on steel substrates. The total thickness of each multilayer coating was 5.4 µm for Cr/CrN, 7.1 µm for Cr/ZrN, 5.5 µm for Zr/CrN and 6.8 µm for Zr/ZrN. The results demonstrate that Cr/CrN and Zr/CrN had the lowest friction coefficients and wear rates among the samples, shown in Figure 19. However, Zr/CrN multilayers showed slightly better tribological performance, as well as the highest hardness (28 GPa) and adhesion strength (>100 N)⁵⁶.



Figure 19 – Cross-section images of as deposited coatings (a) Cr/CrN; (b)Cr/ZrN; (c) Zr/CrN; (d)Zr/ZrN, (e) and wear rates of each multilayer coating⁵⁶.

One investigation compared the wear behaviour of CrN and Cr₂N thick coatings deposited via closed field unbalanced magnetron sputtering using pulsed DC mode¹²¹. They reported that CrN coatings exhibited a denser microstructure than Cr₂N coatings. Conversely, the Cr₂N coatings had smaller grain sizes and lower surface roughness than the CrN coatings despite having the same coating thickness. Additionally, the CrN coating demonstrated low wear rates, unlike the Cr₂N coating, which exhibited low wear resistance and high wear rates¹²¹.

Despite being the most studied materials for accident-tolerant fuel, the ongoing investigation of chromium and chromium nitride coatings remains crucial. Continued research is necessary to optimize these coatings for even better performance, particularly in extreme environments encountered during severe nuclear accidents. The deposition methods can play an essential role in the quality and performance of the coatings. Therefore, the deposition technologies should be understood for the most suitable application.

2.3 Thin film deposition methods

Thin film deposition technologies are important processes when developing advanced coatings for ATF. As discussed previously, chromium-based coatings have gained significant attention due to their excellent properties. As such, the deposition of chromium-based coatings on nuclear fuel rods presents a promising approach for improving the reliability and longevity of nuclear power systems. Therefore, understanding the available deposition technologies is essential.

A thin film is characterized as a material with reduced dimensions – between a few nanometres and several micron-meters – formed by the gradual organization of individual atomic, molecular, or ionic species. Generally, the deposition methods are separated by categories, such as vapour deposition and thermal spray deposition. A typical vapour deposition process occurs in a vacuum environment, in which the coating material is vaporized into atoms, molecules and ions and precipitates on the substrate creating the coating of interest. Vapour deposition techniques are separated into chemical vapour deposition (CVD) and physical vapour deposition (PVD)¹²². On the other hand, a thermal spraying process is characterized as using a powder material that is heated or melted, then these particles are accelerated straight to the substrate. The coating is created from an accumulation of several layers of sprayed materials. The different thermal spray methods are classified according to the particle temperature and velocity, such as warm and cold spray¹²³.

Among the several thin film deposition techniques available, cold spray, and the PVD techniques of arc ion plating, and magnetron sputtering are commonly employed for depositing chromium-based coatings^{15,124}. Each of these techniques offers unique advantages and challenges, making the selection of an appropriate deposition method crucial for achieving the desired coating properties. Moreover, optimizing deposition parameters is essential to enhancing the coating microstructure and further improving performance attributes such as oxidation resistance, substrate adhesion, and wear resistance.

This section will provide a comprehensive overview of the most used thin film deposition technologies in the context of chromium-based coatings for nuclear fuel

rods. Through an exploration of the principles, advantages, and limitations of each technique, as well as insights into parameter optimization strategies.

2.3.1 Cold spray

The cold spray (CS) deposition technique involves ejecting powder particles accelerated by a high-pressure gas stream at supersonic velocities (300 to 1200 m/s). The gas flow conducts the powder though a nozzle featuring a convergent-divergent geometry, which forces the gas to expand and cool down, accelerating the powder to the supersonic speed. The particles collide with the substrate or deposited material at high velocity, forming the coating particle by particle. A schematic illustration is demonstrated in Figure 20. The process began with compressed gas heated to between 100 and 800 °C. Then, this gas stream is conducted to the nozzle, leading to supersonic acceleration. Meanwhile, the high-pressure gas flow is also conducted to the powder feedstock inlet, which is dragged into the gas jet. The combination of hot, high-pressure gas and powder speeds up as it passes through the nozzle, spraying particles onto the substrate at high speed^{125,126}.



Figure 20 – Schematic illustration of cold spray method¹²⁷

The collision between the powder and substrate makes the particles suffer high strain plastic deformation, which is essential for the adhesion and coating arrangement. Therefore, the particles and substrate should present some ductility. Due to that, metallic powders are the most used material. However, composites and ceramics with at least one ductile element are also feasible¹²⁵.

The term cold spray is derived from the observation that the temperature of the final powder/gas supersonic jet typically stays below a few hundred degrees Celsius. Moreover, CS is defined as a solid-state deposition process because the temperature of the driving gas is never higher than the melting point of the material in use^{125,126}.

Some benefits of cold spray relate to it is low temperature process, due to that no drastic phase transformation or oxidation occurs on the particle and substrate during the deposition. Differing from traditional thermal spray methods that melts the material and combines the kinetic and thermal energy, CS offers benefits because it only depends on kinetic energy. In addition, the method is appropriate for temperature sensitive materials since it does not modify the substrate microstructure. Moreover, the CS coatings have high purity, high density, low oxygen content, no grain growth, high hardness, high deposition rate, and high bond strength¹²⁶.

On the other hand, CS also presents drawbacks, such as low ductility, high surface roughness, highly deformed microstructure, and limitations to coat substrates with complex formats or large areas, as the spray beam diameter is relatively small at 10 mm. Also, the adhesion of the coating is closely connected to the plastic deformation. Thus, ceramic substrates have poor bonding strength. Additionally, the propellant gases (helium and hydrogen) are expensive and highly consumed, increasing the process cost¹²⁶.

The main parameters during the deposition process are the nozzle type, propellant gas, gas preheat temperature and pressure, substrate distance, spray angle, travel speed of the spray gun, and powder characteristics (size, shape, and microstructure). The velocity plays a crucial role in achieving high-quality coatings with the cold spray technique. It determines whether the substrate receives enough energy for deformation and ensures proper adhesion of the coating. Usually, to increase the particle speed it is necessary to elevate the upstream gas temperature or use a lighter molecular gas like helium. In addition, the powder shape, size and microstructure impact the coating final result. For example, the particle size and shape especially affect the final speed; irregular shapes and smaller particles are faster than spherical and bigger ones¹²⁵.

The particle temperature, although limited by the melting temperature of the material, is also important. Higher temperature increases the heat transfer during the coating formation and some properties can be affected, such as yield strength

and hardness. Moreover, the particle density and porosity are critical factors that impact the final density and porosity of the coating¹²⁵.

Investigations around chromium coatings using CS for ATF have shown reasonable results. Park *et al.* used irregular shaped Cr powder between 26 and 45 μ m, obtained from mechanical grinding of the bulk material. As a propellant gas N₂ was chosen, the pre-heat temperature was 800 °C at a pressure of 3MPa and a de Laval type nozzle was used to coat Cr on Zr-alloy substrates. The gun traveling speed was 30mm/s and the final thickness was 45 μ m. They reported a high surface roughness and defects, which is not desirable for ATF. Due to that, an extra process – cold pilgering, which is a rolling process – was needed to reduce the roughness and the defects. As already mentioned in this work (Section 2.2.3.3), these coatings demonstrated a significant reduction in burst damage and cracking/spallation. They also claim that Cr-coated cladding using CS have an excellent steam oxidation resistance at 1200 °C for a 1h test, and interdiffusion between the coating and substrate was not reported¹¹³.

Other studies on CS Cr coatings also used irregular Cr particles with a size of about 44 µm, helium was used as a propellant gas, the pre heat temperature was 675°C and the pressure was 3.15 MPa. According to the authors, the CS Cr coatings were nonuniform and heterogeneous in comparison with PVD and 3D laser coatings. Even though, they noticed good oxidation resistance in 500 and 1200 °C steam tests. However, when they assessed the mechanical performance, the results were discouraging. In an oscillation test using loads from 20 to 1800 N, 3-4 Hz frequency, and water environment at 300 °C, the Cr-coated samples exhibited early cracking when compared to the uncoated samples. Also, the behaviour of chromium-coated tubes under creep conditions for 120 hours at 360 °C was similar to that of uncoated ones. In burst tests where the coated tubes were subjected to internal pressures of 4 MPa at 800 °C in an argon environment, the time until bursting was five times shorter with smaller openings compared to the bare substrates. Additionally, the surface roughness (Ra) of the coatings were higher than the original substrates; 0.41 and 0.32 µm, respectively. The authors claim that mechanical results can be improved by cold spray coatings with uniform thickness, and more adhesion strength of the coating onto the substrate.

Yeom *et al.* analysed several investigations of the cold spray technique in nuclear applications. They claim that the main difficulties to apply the CS involves technical and cost concerns, such as⁴⁰:

- Components with complex geometries may require part and/or spray gun manipulation since CS is a line-of-sight process.
- Cold spray coatings have an inherently rough surface, which would require a polishing step after deposition.
- Cold spray coatings may be less ductile due to their work-hardened state.
- Obtaining the desired mechanical properties may require postdeposition heat treatments with near-net shapes.
- Increased gas consumption and high prices.

2.3.2 Physical vapour deposition (PVD)

Physical vapour deposition involves the evaporation or sputtering of atoms or molecules from a solid source (target). These particles then travel through a low-pressure, vacuum, and gaseous chamber, toward the substrate where they condense, forming a thin film. To operate PVD successfully, the path from the target to the substrate should be as free as possible from collisions with gas molecules. This necessitates maintaining the chamber in a range between high (0.1 to 10⁻⁵ Pa) and ultra-high vacuum (> 10⁻⁵ Pa). PVD is a versatile technique, capable of depositing a variety of materials, including inorganic and some organic compounds, formed by a pure element, alloys or compounds. Moreover, this technique can create single material or multilayer coatings. Importantly, it does not produce hazardous materials during the process^{128–130}.

The PVD method can be classified into four main processes:

• Thermal evaporation: the material is heated within a vacuum to an elevated temperature, causing it to either evaporate or sublime. The
vapour then condenses onto the substrate, where it solidifies and forms a thin layer. Generally, a vapour pressure of over 1 Pa is necessary to achieve satisfactory deposition rates¹²⁸. This is a low energy process with corresponding porous columnar structures and poor properties.

- Arc evaporation: utilizing a high current and low voltage, this method employs an electric arc under a low-pressure gas environment to erode the solid cathodic electrode through a moving arc or to melt and vaporize the anodic electrode. Then, the vaporized atoms move across through a dense electron cloud, they ionize and are accelerated by an electric field toward the substrate. Reactive gases can be introduced to form oxides or nitride coatings¹²⁸.
- Ion plating: a source of high-energy ions bombards the substrate, removing atoms/molecules prior to deposition and densifying the structure of the film during deposition. The ions for the bombardment can be extracted from a plasma (see 2.3.4) environment or introduced in a separated source in a vacuum environment. In general, the ions used for bombardment are an inert gas or a reactive gas (reactive ion plating). Moreover, the methods to vaporize the target material to produce the coating flux could be evaporation, sputtering, arc vaporization, or even a decomposition of a chemical vapour precursor (chemical ion plating)¹³¹.
- Sputter deposition: the target is negatively charged, which accelerates electrons away from the target, where they collide with inert gas atoms and ionise them. Then, these positive ions bombard the target and sputter the atoms from the target surface. The ejected atoms are deposited over the substrate, creating atom-by-atom the thin coating¹³². Magnetron sputtering is an extension of the basic sputtering process with greatly improved deposition rates and film properties.

As mentioned, arc ion plating and magnetron sputtering are, among the PVD technologies, the most used for ATF applications. Due to that, as one of the focuses of this work, magnetron sputtering will be detailed in section 2.3.2.2. In addition, arc ion plating will be described as a comparison of a competing technique.

2.3.2.1 Arc ion plating

The arc ion plating (AIP) method uses high-energy electric arcs to vaporize the target material. Initially, a low-voltage and high-current pulse is applied on the target material (cathode) to induce an electric arc between the cathode and anode. Consequently, this arc spot locally heats the target material, which vaporizes. In addition, the arc also ionizes the vapour in the chamber, forming a plasma with metal ions and electrons. Also, a negative bias voltage is applied on the substrate. The resulting electric field accelerates the metallic ions into the substrate, depositing a thin film. Compared with other ion plating methods, arc ion plating has a dense plasma and the highest rate of metal ionization. Multiple cathodes can be arranged within the chamber, and this configuration is referred to as multi-arc ion plating^{133,134}, as illustrated in Figure 21.



Figure 21 - Schematic illustration of multi-arc ion plating¹³⁵.

The main advantages of arc ion plating involve the formation of very dense, hard, uniform coatings and with high adhesion to the substrate. The

process requires low temperatures, no post-treatment is necessary, presents a fast deposition rate, and does not produce any hazardous substances^{124,130}. However, in addition to transforming directly into metal vapour plasma, the high energy density also causes many droplet ejections. These droplets are inevitably deposited on the surface and incorporated into the coating. Consequently, a very rough surface is formed, which decreases the overall performance of the coating and represents the primary limitation of this technology. Furthermore, the high current vacuum arc discharge requires target materials with excellent electrical conductivity. Therefore, materials with high or low melting points and poor mechanical strength are unsuitable for arc ion plating^{130,136}.

The coating characteristics are closely connected to the deposition parameters: target-substrate distances, bias voltage, target power, chamber temperature, substrate holder rotational speed, target current, and gas pressure¹³⁷. The deposition rate tends to increase with a rising arc current. However, extremely high currents could result in arc instability and coating defects. The bias voltage applied on the substrate can also have a relevant effect on coating quality and macroparticles. Additionally, a target with a large area is favourable for creating a denser plasma in a constant arc current, which enhances the surface quality and performance. Concerning the droplets, a method to reduce than is to improve the cathode configuration and use a macroparticle filter¹³⁸.

For instance, Lan *et al.* analysed the influence of arc current and bias voltage on the properties of AlCrN deposited using arc ion plating with a large target. They found that a higher current leads to a higher deposition rate. However, the coating hardness and wear behaviour worsen because of the influence of macroparticles and coating density. Regarding biasing the substrate, the deposition rate was not significantly affected. On the other hand, the hardness, wear resistance and corrosion resistance increased from -50V to -100V bias, but dropped from -100V to -150V bias¹³⁸.

Also, testing the parameter's effects on coatings using AIP, Wan *et al.* studied the influence of nitrogen pressure and bias voltage on the properties of CrN coatings. The N₂ pressure increase resulted in higher deposition rates, but more macroparticles were observed and they related this finding to the low melting point of the nitride produced on the target material. Concerning bias, the results showed a preferred texture change from (200) to (220) when the bias was elevated.

In addition, the deposition rate first increased with increasing bias but then dropped quickly with higher bias values. They also reported that by elevating bias voltage, the macroparticles significantly decreased due to the ion bombardment and electrical repulsion force on the substrate plasma surroundings¹³⁷.

Some recent investigations assessed the oxidation behaviour in steam and high temperatures of Cr coating on Zr alloys deposited by AIP. Liao *et al.* coated Zr-4 plates using multi-arc ion plating technology, applying a -150V bias voltage, heating the substrate at 250 °C, and using an arc current fixed at 100A to obtain a 7 μ m film. Then, they analysed the oxidation performance in a steam environment for 30 minutes at 1100 °C, 1200 °C, 1300 °C, and 1400 °C. They found that the Cr coating demonstrated excellent oxidation resistance and drastically reduced the weight gain of the Zr alloys at 1100 and 1200 °C. While at 1300 °C, the Cr₃O₂ formed layer starts to suffer signs of degradation, such as bubbles and voids. Then, at 1400 °C, the Cr coating no longer protects the substrate. Figure 22 shows the weight gains of the Cr-coated samples in comparison with the bare Zr-4, and clearly at 1400 °C the coated sample presented a concerning performance¹³⁹.



Figure 22 – The weight gains of Cr-coated produced by multi-arc ion plating and uncoated Zr alloy after steam oxidation and increasing temperatures¹⁴⁰.

Similarly, Xiao *et al.* investigated Cr coatings produced by multi-arc ion plating, applying -100V bias voltage, substrate heating up to 400 °C, and an arc current of 80A to achieve a thickness of 13 µm. They tested this sample's oxidation

behaviour in an air atmosphere for between 1 and 4 hours at 1000 °C, 1100 °C and 1200 °C. The results showed that the chromium coating could protect after the 4h test at 1000 and 1100 °C, while at 1200 °C, it protected the substrate for 1h.

Regarding the irradiation tests at normal operation and LOCA conditions, a study tested irradiation under corrosion and oxidation environments of Cr coatings deposited using arc-ion plating. They produced different coatings varying the deposition parameters. In general, they claimed that after post-irradiation oxidation/corrosion tests, the Cr coatings demonstrated a good performance under normal and LOCA conditions until 1000 °C. However, at 1200 °C, a rapid oxidation of the Cr coating was observed¹⁴¹.

About wear resistance of Cr coatings produced via arc-ion plating, J. Wang *et al.* conducted an interesting study on the temperature influence on the fretting wear protection in high-temperature and pressurized water environments²⁴. The chromium was deposited on Zr-4 tubes using a multi-arc ion plating process, the substrate was heated up to 250 °C, a bias voltage of -120V was applied and the arc current was kept at 120A, leading to a final thickness of 8 μ m. The samples were submitted to a unique autoclave equipment with a high-temperature, high-pressure, water environment, and a fretting test device installed inside the vessel system. The test was conduct in pressurized water at room temperature (RT), 90 °C, 260 °C and 315 °C. The normal load used was 20N, the displacement amplitude set to 100 μ m, the frequency at 5Hz, and the fretting wear cycles (N) was 4 x 10⁴. The samples were immersed for 4 hours in high-pressure and high-temperature water environment before the test.

Their findings indicate an enhancement in the wear resistance of the Crcoated tubes compared to the bare zirconium tubes. Particularly, a significant reduction in wear volume and depth was observed at higher temperatures, specifically at 260°C and 315°C, which closely align with the normal operating temperatures of the reactor²⁴, as can be seen in Figure 23.



Figure 23 – (a) Wear volume, (b) maximum wear depth, and (c) 3D morphology of the worn surfaces of Cr-coated and uncoated Zr-4 tubes via multi-arc ion plating²⁴.

As presented in the bar chart, the reduction in wear volume reached nearly 99% at 260°C and 315°C. In addition, it was noticeable how harmful the wear was at the higher temperatures for the uncoated tubes, while the wear resistance was significantly lower for the Cr-coated samples at the same temperatures, 260°C and 315°C. Therefore, under normal operation conditions, the Cr-coatings perform better than the Zr alloys in terms of wear behaviour. They also reported that temperature influences the wear mechanism of the Zircaloy cladding. The samples transitioned from delamination and abrasive wear at low temperatures to adhesive and abrasive wear at high temperatures during the temperature increases²⁴.

2.3.2.2 Magnetron sputtering

Sputtering is defined as the ejection of atoms through the collision of energetic ions accelerated towards a solid surface, as illustrated in Figure 24. Compared to the evaporation process, sputtering is more widely used because it presents some advantages, such as deposition of high melting point or dielectric materials directly from a solid target, source material staying relatively cold throughout the deposition process, fabrication of ceramic material with a specific stoichiometry using elementary target material accompanied by a reactive gas (N₂ and O₂) or using a ceramic target. In addition, extensive surfaces can be coated with high uniformity across their lateral dimensions, and the sputtering source can be oriented in any direction^{122,129}.



Figure 24 – Illustration of a physical sputtering mechanism¹²⁹.

The sputtering coating process occurs inside a chamber at high vacuum, and a target (cathode) is placed in front of the substrate. Then, some gas, usually argon, is introduced in the chamber and a glow discharge plasma is initiated by connecting a high negative voltage supply to the target. Electrons are accelerated away from the target and collide with argon atoms and ionise them. The positive argon ions are then accelerated towards the target and hit the target with sufficient energy to remove or 'sputter' target atoms from the surface. These atoms travel across the chamber and are deposited on the substrate¹⁴².

Various sputtering systems, such as DC diode, RF diode, and magnetron diode, are employed in practical applications. The most straightforward system is

the DC diode sputtering, in which a direct current voltage of a few kV is applied to the cathode. The negative charge on the target accelerates away the electrons, resulting in ionisation of argon inserted in the chamber. A glowing plasma is created between the cathode and anode due to accelerated electrons exciting the gas molecules and emitting visible light. Then, the sputtering process is initiated with the Ar+ ions attracted to the target. During the process, secondary electrons are also released from the target surface to help sustain the plasma^{129,143}.

When an insulating target material is used in DC sputtering, it is not possible to strike a discharge. To address this, a radio frequency (typically 13.56MHz) voltage can be used on the target material to drive the plasma. Only electrons can respond to the changing field at the target at RF frequencies, which results in the equivalent to a DC voltage being established at the target, which allows positive argon ions to be attracted to the target and sputtering to occur¹²⁹.

DC diode sputtering has some drawbacks, including low deposition rates, target poisoning when using reactive gases, heating of the substrate caused by electrons accelerating away from the cathode, and the target material must be electrically conductive¹³².

The magnetron sputtering technology is a significant advancement over the DC sputtering process. In this process, magnets are strategically placed behind the targets. The magnetic field lines originate at the centre of the cathode, cross the target surface in an arc route, and enter the cathode at its annular end. This arrangement, as shown in Figure 25, ensures that the magnetic field lines are organized to appear approximately parallel to the target surface in the regions between the inner and outer magnetic arrays¹³².



Figure 25 – Illustration of the DC planar magnetron discharge in a sputtering configuration¹³².

The electrons in the glow discharge obey the Lorentz force (or electromagnetic force), which is a combination of forces from the electric (E) and magnetic (B) fields. When a change (q) is in motion in both magnetic and electric fields, the total force of the particle is driven by the Lorentz force (Equation 2)¹⁴⁴.

$$\vec{F} = q(\vec{E} + \vec{v} \times \vec{B})$$
 Equation 2

Then, the electron follows a helical path in a uniform magnetic field, moving perpendicularly to both magnetic and electric fields, also known as "E X B drift" (Figure 26). The ions are not significantly affected by the magnetic field because they are much heavier¹⁴⁴.



Figure 26 - (a) Trajectory of an electron moving with a speed v_{II} parallel to a magnetic field B, orbiting the magnetic field lines at a radius r_g . (b) Trajectory of an electron moving in a perpendicular magnetic and electric fields E, causing the drift with velocity v_E . (Adapted from J.A Thornton, 171 (15), 1978).¹⁴⁵

The magnetic field applied in a magnetron prolongs the lifetime of electrons escaping from the cathode and traps them in the cathode's vicinity. Additionally, the ionisation caused by the electrons colliding with the argon atoms occurs near the cathode since the electrons are confined in the same area. Therefore, the plasma density is several orders greater than the DC glow discharge. Also, magnetron sputtering allows lower gas pressures as the sputtering process becomes more efficient with the magnetic trap^{132,142}.

The combination of all these effects makes the magnetron sputtering more attractive, producing higher-quality films at higher deposition rates. Since the development of magnetron sputtering, it has been the most employed method for the deposition of thin films. It is a well-established technology in the surface coatings industry and has several advantages, including producing adherent, dense and homogenous coatings. In addition, the coatings have similar properties to the bulk material equivalent²¹.

Depending on the configuration of the magnetrons, the coating process may be enhanced. There are two possible configurations: balanced and unbalanced magnetrons. The balanced case is the conventional configuration, and it uses the same magnetic field strength on both poles of the magnetic array inside the magnetron (Figure 27.A). Thus, the magnetic field lines are limited to the target vicinity, creating a dense plasma. In this configuration, the ion current is high near the magnetron and weak in the substrate region. On the other hand, using different field strengths in the magnetrons, the magnetic field becomes unbalanced. There are two different types of unbalanced magnetron which have an influence on the magnetic flux. In the type I the outer magnets are weaker than the inner magnets and the field lines are directed to the chamber walls (Figure 27.B). However, the type II is the opposite, the outer magnets are stronger than the inner ones, and consequently the magnetic field lines are directed toward the substrate vicinity (Figure 27.C). Applying the unbalance type II is advantageous because it significantly increases plasma density around the substrate and improves the ion bombardment on the sample during deposition, which in turn improves the film structure and properties.



Figure 27 – Illustration of balanced and unbalanced magnetrons configurations¹³².

When there is a system with more than one magnetron, the magnetic field can be adjusted with either identical or opposite polarities. The first configuration in known as mirrored and the field lines are directed toward to chamber walls, therefore, there is a low plasma density around the substrate (Figure 28.C). The second configuration is called closed field, the field lines between the magnetron are linked and surround the substrate, which increases the plasma density in the substrate region, again leading to better film properties (Figure 28.A and Figure 28.B)²¹.



Figure 28 – Illustration of unbalanced magnetrons configurations²¹.

The magnetron sputtering discharge can be operated in direct current (DC) mode or pulsed DC mode. In the first case, a constant current is applied. However, positive ions can accumulate on the target surface, which causes arcs and decreases further sputtering (Figure 29.A). A phenomenon known as "target poisoning" can also occur during reactive deposition, where insulating layers of the reactive product concentrate in some parts of the target. Thus, charged up areas results in an arc breakdown¹⁴³.

A solution for this problem is the pulsed DC mode, in which the voltage varies from "pulse-on" to "pulse-off" modes. In the pulse-on period a negative voltage is applied on the target (Figure 29.B), and in the pulse-off period the negative voltage is turned off for some microseconds, or a small positive voltage is applied (Figure 29.C). As a result, the positive charge accumulated on the surface is neutralized, preventing arcs, and increasing the efficiency of ion attraction to the cathode. The pulsed magnetron sputtering is useful to improve process stability and reduce the number of defects in the coatings^{21,132,143}.



Figure 29 – Illustration of a pulsed DC sputtering mode¹³².

The periodical switching of the power voltage can be set at frequencies from 20 to 350 kHz. In contrast to radio frequency methods, within this frequency range, both ions and electrons can track the cyclical shifts in electrical potential occurring at both the target and within the plasma¹⁴³.

To completely suppress the arc, the pulse parameters should be appropriate for the operation conditions of each material, because the arc can also happen with incorrect settings. Studies had shown that the most important factor affecting the arc rate is the duty, which is the ratio of the pulse-on period to the entire pulse cycle¹⁴³. The duty cycles can variety from 50 to 90%. Several investigations demonstrate that arc suppression results in mainly defect-free coatings, as well as fully dense structures, improved durability and optical properties, and smoother surfaces^{146–151}.

Biasing the substrate is an option during the coating process to produce denser structures. Applying a negative voltage on the substrate accelerates the particles towards it, specifically positive ions, but energetic neutrals that were ions, which were subsequently neutralised due to collisions in the plasma, will also bombard the substrate. This creates knock-on implantation, which is when an energetic ion transfers enough energy to atoms in the film, causing them to be implanted beneath the film's surface. Also, the higher energy on the substrate accommodates the surface atoms deeper into the structure creating a denser coating that may be beneficial regarding the oxidation and mechanical resistance. However, excessive biasing can result in high film stresses, with possible cracking and delamination of the film. Therefore, the appropriate bias value should be investigated for each material and application ^{23,152,153}.

Reactive sputtering is a widely used process for producing coatings of compounds on an industrial scale, such as oxides and nitrides. It involves the introduction of a reactive gas (O_2 or N_2) into the system in addition to the Ar gas. The metal is sputtered from the target, and a precise amount of reactive gas is introduced into the chamber to form the desired compound on the substrate. Understanding this process is crucial for achieving the desired results^{142,154,155}.

In order to produce a stoichiometric product with a satisfactory deposition rate, the balance between the sputtered metal atoms and the appropriate reactive gas rate should be controlled. However, controlling a constant metal sputtering rate is a complex task. Unlike a metallic coating formation, the metal removal rate in a fixed power to the magnetron sputtering is not constant. The oxygen or nitrogen introduced to the chamber reacts with the substrate, chamber wall, and the target as well. The compound can be formed on the target surface, causing what is known as target poisoning^{154,156}.

The target poisoning leads to an inherent instability and a non-linear response to the changes in operating parameters. A hysteresis curve characterizes the nonlinear behaviour. Thus, the progression of the parameters such as the deposition rate, discharge voltage or gas partial pressure are described according to the reactive gas flow. Figure 29 illustrates an example of Ti sputtering in an Ar and O₂ environment and its respective hysteresis curve according to (a) the deposition rate, (b) discharge voltage or (c) oxygen partial pressure¹⁴².



Figure 30 – The evolution of process parameters during reactive sputtering of titanium (Ti) in an argon/oxygen (Ar/O2) atmosphere¹⁵⁷.

As can be seen in Figure 30, when the reactive gas flow rate is low, the deposition rate is high because the reactive gas is consumed at the substrate but is not sufficient to also react with the cathode. This region is defined as "metal mode." During the increase of the reactive gas flow rate, the sputter yield falls sharply due to the compound formation on the target, transitioning to what is called "poisoned mode." This transition is signalized by the arrows in the example charts of Figure 30. Compounds exhibit hysteresis when their sputtering rate is different to their pure metals^{142,155}.

Moreover, controlling the reactive gas's partial pressure or discharge voltage makes it possible to maintain the required amount of gas atoms to form a stoichiometric film according to the gas consumption in the reaction. For example, if the reactive gas is introduced at a constant rate, the partial pressure of the reactive gas can increase rapidly. The reason is that the deposition rate drops once fewer gases are being consumed in the reaction. On the other hand, if the reactive gas flow is decreased after the partial pressure is increased, the partial pressure (or discharge voltage) will not return through the same course as the way up. Thus, the reactive hysteresis loop is formed¹⁴².

The system should be operated in the transition regime between metallic and poised modes to deposit the stoichiometric film at high rates. Significantly increasing the pump speed can reduce hysteresis behaviour. However, this method may not be cost-effective. Controlling the reactive gas flow with a feedback system has been shown to be an effective method of forming compounds with a relatively high deposition rate¹⁴².

Studies have shown promising results in ATF for Cr-coatings on Zr alloys using the magnetron sputtering technique. For instance, Huang *et al.* used direct current magnetron sputtering to coat Zr-4 alloy plate with Cr. During the deposition the substrate was heated to 400 °C, a bias voltage of -100V was used, and final thickness of the chromium layer was about 15 μ m. Scratch testing demonstrated an adhesion strength of the Cr coating of more than 100 N. Furthermore, the same samples were submitted to high temperature oxidation tests in an air environment at 1200 °C for 3 h and presented relevant results: Firstly, the Cr-coatings had no damage, such as cracking or spalling off. Secondly, the chromium protective oxidative layer – Cr₂O₃ – was found, as well as a residual Cr layer, both around 4 μ m. And finally, the Zr alloy was not oxidized in this test ¹¹².

A most recent study conducted by Dong Wang *et al.* tested further conditions of Cr-coatings in steam oxidation at a typical temperature selection of accident conditions: 1000, 1100, 1200, and 1300 °C. Magnetron sputtering was used to coat Zr-1Nb alloy cladding tubes, and the authors reported a dense film without defects and a thickness of around 11.8 μ m. The oxidation duration varied according to the temperature and observed results. The visible characteristics of the Cr-coated samples after the oxidated test¹⁵⁸, test duration and temperature are shown in Figure 31.



Figure 31 – Visible characteristics of the Cr-coated Zr alloy via magnetron sputtering after the oxidated test perfumed at varied periods and temperatures¹⁵⁸.

The oxidized samples were submitted to several analyses, including weight gain, surface and cross-section morphology, macroscopic appearance, evolution of the Cr_2O_3 layer and ZrO_2 interlayers. Therefore, the authors concluded that the Cr films deposited via magnetron sputtering can sustain the oxidation resistance for more than 6h at 1000 and 1100 °C under a double-sided oxidation test. On the other hand, at 1200 and 1300°C, the coating experienced degradation in long-period tests. In addition, after degradation, the coating continues to somewhat prevent the oxidation of the Zr substrate at 1200 °C, but it nearly loses its protective effect at 1300 °C¹⁵⁸.

Regarding fretting wear tests, an up-to-date investigation assessed the wear behaviour of chromium depositions onto Zr-1Nb via radio frequency magnetron sputtering. A bias voltage was applied, and the chromium final thickness was 15 μ m. They studied the tangential displacement's influence on the coating's fretting

wear resistance in a dry, room temperature, and atmospheric pressure environment. In the fretting test, the displacement was changed from 40 to 120 μ m. The normal load was 50N, and the frequency was 10 Hz. According to the authors, the amount of removed material and maximum wear depth increased proportionately to the tangential displacement. The maximum wear depth results observed in this study are presented in Figure 32. As demonstrated, after 100 μ m displacement, the coating was worn until subtracted¹⁵⁹.



Figure 32 – Maximum wear depth vs. the tangential displacement of Cr coatings onto zirconium alloys¹⁵⁹.

However, in general, they observed that the Cr coating can lower the wear on the cladding tube. An interesting observation was that when the coating is completely worn, they noted that the volume of material removed shows a significant increase. Additionally, they reported that in smaller displacements, a three-body phenomenon may obstruct the wear in the system. At large displacements, the wear chips are easily discharged, which worsens the wear situation¹⁵⁹.

It is essential to highlight a comparison reported on the review study conducted by Yang *et al.* on chromium coated Zr alloys, where different deposition technologies of Cr coating were evaluated. They claim that magnetron sputtered coatings presented a reduced oxidation rate compared to other methods, such as cold spray, vacuum arc plasma deposition, arc ion coating, etc¹⁵.

2.3.3 Vacuum

Vacuum is a prerequisite to produce high quality films in various coating technologies, including magnetron sputtering deposition which is the focus of this work. Vacuum refers to a space devoid of gas molecules and characterized by lower pressures than the ambient¹⁶⁰.

The vacuum technology empowers vacuum coating for the following reasons: first, it creates a low particle density environment, leading to a long mean free path for the particles to travel towards the substrate with minimum collisions. Second, it prevents undesirable reactive deposition by eliminating the maximum residual vapour species. Third, it provides a specific pressure (or partial pressure) of reactive gases to control the films characteristics and stoichiometry. Finally, it facilitates the ion acceleration in an electric field throughout the sputtering process or property modifications on the deposited coating¹⁶¹.

Vacuum can be classified in different ranges, depending on absolute pressure:

- Atmospheric pressure: 1x10⁵ Pa;
- Low vacuum: 1x10⁵ 1x10³ Pa;
- Medium vacuum: 1x10³ 1x10⁻¹ Pa;
- High vacuum: 1x10⁻¹ 1x10⁻⁷ Pa;
- Ultra-high vacuum: 1x10⁻⁷ 1x10⁻¹⁰ Pa.

2.3.3.1 Vacuum measurement

Measuring pressure in vacuum systems is complex and demands multiple devices to indicate different pressure stages. An accurate pressure measurement is crucial to determine a condition for reproducibility. In order to improve the process control and quality of coatings produced, it is necessary to select the correct type of vacuum gauge for the process¹⁶¹.

Pirani gauge

The Pirani gauge, designed for low vacuum applications, operates on the principle of thermal conductivity. It features a metal filament that is heated, and

heat is dissipated due to molecule collisions. As the pressure increases, more species collide with the filament, leading to heat loss. Conversely, as the pressure decreases, the number of collisions decreases, causing a temperature rise in the filament. This filament, with its electrical resistance that varies with temperature, allows for the conversion of resistance readings into pressure values.

It's crucial to note that the Pirani gauge is sensitive to different gases. This sensitivity arises from the fact that different gases absorb varying amounts of heat from the filament due to their masses. Therefore, it's essential to calibrate the Pirani gauge based on the gas being used. The gauge is effective within a pressure range of 0.13 to 133 Pa¹⁶¹.

• Penning gauge (cold cathode ionisation)

The Penning gauge is composed of an anode and a cathode inside a magnetic field. Then, a potential of about 2kV is applied to the cathode, producing a glow discharge. A glow discharge is a phenomenon that occurs in a gas-filled space in an electrical field applied through it. The molecules are ionised, and the processes create a self-discharge identified by a visible light emission.

This gauge, therefore, uses the current produced by a glow discharge to measure the system pressure. The positive ions generated are collected at the cathode, creating an electric current. The current magnitude is proportional to the pressure of the gas in the chamber. The electric current is measured and converted into a pressure reading.

The Penning works under a specific condition. If the pressure is too low or high, no glow discharge can be produced. This is because either too many molecular collisions inhibit the glow discharge, or collisions are insufficient. The gauge is effective within a pressure range of 1.3 Pa to 1.3 mPa¹⁶¹.

Capacitance manometer (Baratron gauge)

The capacitance manometer or MKS Baratron® gauge is an accurate instrument operating on the fundamental principle of capacitance. It consists of two metal plates positioned parallel with a small gap and a diaphragm placed between

them. When a voltage is applied, a capacitor is formed between the plates/electrodes.

The diaphragm is exposed to the gas whose pressure is being measured. The different gas pressure during the chamber evacuation exerts a different force on the diaphragm, leading to a deflection. The deflection changes the gap between the capacitor plates, which modifies the system's capacitance. The capacitance is inversely proportional to the pressure exerted on the diaphragm.

Baratron gauges have advantages in high accuracy and a wide pressure range. They measure the absolute pressure and do not depend on the type of gas used. This gauge is effective within a 1 Pa to 20 kPa pressure range¹⁶¹.

2.3.3.2 Vacuum production (Pumps)

Pumps are integral components in the evacuation chamber system that work in collaboration and following a logical sequence. At the outset, the pump-down process commences in a low vacuum, a stage where a high volume of gases with a low mean free path behaves like a cohesive fluid or a viscous flow.

Positive displacement pumps, such as the rotary pump, are the tools of choice at this stage. As the gas removal progresses, the system undergoes a significant transition, evolving into a high vacuum. This transition is marked by a decrease in collisions, a rise in the mean free path, and a shift from a viscous to molecular flow. From this point onwards, diffusion or turbomolecular pumps take over, underscoring the importance of this transition in the process¹⁶².

Rotary vane pump

The rotary vane pump is among the most popular roughing pumps for low vacuum. When combined with high vacuum pumps, these are roughing or backing pumps. It consists of a cylindrical compartment with a rotor, inlet, and outlet space for the gas flow. The rotor spins, drawing the gas into an expanding space and then moving to a contracting space before exhausting it to the atmosphere, as illustrated in Figure 33. This loop repeats for numerous times, leading to a pressure decrease to the low vacuum range. Rotary pumps are very efficient and relatively

fast for achieving low vacuum. However, when the molecular regime flow is reached, a pump with higher potential should be used¹⁶².



Figure 33 – Schematic illustration of a rotary vane pump¹⁶².

• Diffusion pump

The diffusion pump is a momentum transfer type of pump which uses a highspeed stream of vapour to achieve a high vacuum. In practice, this pump operates by heating the pump fluid (low vapour pressure oil) and turning it into vapour. The oil vapour rises and passes through nozzles in the central part of the pump. These nozzles propel the steam downwards at high speeds. Then, the high-speed vapour jets collide with gas molecules, transferring momentum and carrying them towards the backing pump, where they are expelled from the system. After that, the vapour condenses on the cooled parts of the pump, subsequently being directed to the reservoir, where it is evaporated again. An illustration of the diffusion pump is demonstrated in Figure 34.

Depending on the vacuum configuration, diffusion pumps usually reach a pressure down to 10⁻⁸ Pa. This pump's main advantages are its simple maintenance, low running cost and robustness. However, the drawbacks could involve sample contamination by oil and a cooling water system.



Figure 34 – Schematic illustration of a diffusion pump¹⁶².

• Turbomolecular pump

The turbomolecular pump is also a high vacuum pump belonging to the momentum transfer group. This pump comprises a shaft rotating at high speed and multibladed rotors. The angle-shaped blades of the rotors capture the gas molecules at the upper stages and push them down to the lower stages. As the gas molecules pass through the lowest stage of the pump, they are usually piped to the roughing line through the exhaust. A turbomolecular pump is illustrated in Figure 35.

This pump can also be used to achieve pressures around 10⁻⁸ Pa. Turbomolecular pumps' positive points include easy operation, low maintenance, a robust system, and no sample contamination. Their negative points are that this pump is intolerant to particle contamination and is more fragile due to the mechanical moving parts¹⁶².



Figure 35 – Schematic illustration of a turbomolecular pump¹⁶².

2.3.4 Plasma

Plasma is an essential element of some deposition processes. Plasmas' unique properties, such as their ionisation, global neutrality, electrical conductivity, and electromagnetic response, make them important for material processing.

Plasma, a partially ionised gas, is a complex mixture of free electrons, ions, atoms, and molecules. It is characterised by an approximately equal number of positively and negatively charged species. This unique state of matter, known as the fourth state, defies the traditional definitions of solid, liquid, and gas. Plasmas are typically formed in a vacuum through thermal (hot plasma) or electrical (cold plasma) methods. They can be further classified based on their charge density, average electron energy, and degree of ionisation¹⁶⁰, as illustrated in Figure 36.



Figure 36 - Plasmas sorted according to their electron energy and electron density¹⁶⁰.

The degree of ionization (α) is calculated with the Equation 3, n_e is density of electrons and n_n is the neutron atoms density.

$$lpha = rac{n_e}{n_e + n_n}$$
 Equation 3

In materials processing, the most common type of plasma is the glow discharge plasma. This type of plasma is formed when a DC or RF electric field is applied to a specific volume of gas. The discharge generation is due to the acceleration of the primary electrons with the electric field in the cathode surroundings.

During plasma creation, the gas molecules are ionised by electron collision, creating cations. The electrons energy may be superior to the gas molecule ionisation energy. The cathode is bombarded with positive ions, leading to the formation of secondary electrons, which later also ionise the gas. Thus, a stable plasma is established¹⁶⁰.

2.3.5 Thin film growth

In any PVD process, the properties of the resulting film are intricately linked to various factors influencing its growth and characteristics. These factors include deposition conditions, outgassing phenomena, surface morphology, and chemical interactions at the substrate interface. Understanding how thin films initially form is important because it helps to customize their properties for different uses. Therefore, this section discusses the fundamental mechanisms, initial growth and structure zone models of thin film growth.

2.3.5.1 Nucleation and initial growth

A thin film growth process can be summarized as involving a statistical nucleation process, growth of three-dimensional nuclei controlled by surface diffusion, and the development of a network structure followed by its filling to create a continuous film.

In details, the formation of thin growth occurs in a few phases^{163,164}:

- 1) First, the atoms reach the substrate with a relatively high kinetic energy, however, after a few vibrational periods, they become thermally accommodated at the substrate. Then, they are physically absorbed.
- 2) Next, the adsorbed atoms (adatoms) diffuse over the substrate to find thermal equilibrium position or be desorbed from the surface. Usually, the diffusion is conducted by substrate temperature, adatoms' kinetic energy, and integration between the materials. Once the adatoms locate in the substrate, the nucleation begins, which is the initial stage of the particles arrangement to form clusters or nuclei. The nucleation areas are usually lattice defects or atom steps.
- 3) Afterward, the cluster grows seeking for thermodynamic stability. The sum of volume free energy $(\frac{3}{4}\pi r^3 \Delta G_V)$ and surface energy $(4\pi r^2 \gamma)$

governs the total free energy (Δ G) of a cluster formation. Where r is the clusters radio, γ is the interfacial energy per unit area, and ΔG_V is the change in free energy per unit volume.

Then, a delicate equilibrium between these two energies is established, gradually leading to cluster stability. It's important to note that this stability is only achieved when the cluster exceeds its critical size. Figure 37 presents a diagram of the total system free energy of the cluster formation, conceptualizing the cluster as a spherical solid in a homogeneous fluid.



Figure 37 – Schematic diagram of the system free energy of cluster formation¹³¹.

4) Subsequently, the stable clusters continue to expand, incorporating more clusters and adatoms. Eventually, the clusters begin merging with one another, creating islands, and reducing the substrate surface area. 5) Finally, the film structure transitions from isolated islands to a porous network. Channels and gaps are filled, resulting in a fully continuous film.

The nucleation stages described above are illustrated in Figure 38.



Figure 38 – Schematic illustration of the (a) phases during the nucleation and (b) the three film growth modes¹⁶⁵.

After the nucleation stage, three initial film growth modes can be observed depending on the interaction energies between the substrate and the source material atoms (see Figure 38)¹⁶⁶:

- Island type (Volmer-Weber): it is a 3D growth process that develops when the atom-to-atom synergy is greater than between the substrate and adatoms. Then, the clusters aggregate to each other, forming islands that integrate and evolve to a continuous film. Metals and semiconductors often grow islands on gas-metal-compounds like Ag, SiO₂, NaCl, or TiO₂ ^{167,168}.
- Layer type, (Frank-van der Merwe): is a 2D growth mode in which adatoms assemble in layers over the substrate and the film is created by levels of atoms stacking in these layers. The interaction between substrate and atoms is greater than between the adatoms. Typical layer growth examples include contamination-free homoepitaxial growth of semiconductor films,

but low-melting-point metals can also grow on high-melting-point metals^{169,170}.

 Layer plus island type, (Stranski-Krastanov): this growth mode begins with the formation of a few monolayers, then islands are preferable due to an unfavourable growth of monolayers. It occurs as a result of strain relaxation mechanisms (strain-induced roughening)^{171,172}. Systems containing metalmetal, metal-semiconductor, and semiconductor-semiconductor have shown this type of growth^{173–175}.

2.3.5.2 Structure zone model of growth.

The continuous nucleation of atoms on the already deposited material leads to film growth. Both nucleation mode and film growth influence several film properties, including film density, surface area, grain size, and microstructure. The microstructure has shown a partial influence on important coating properties, such as hardness, wear resistance, electrical conductivity, corrosion resistance, refractive index, and even the film's colour¹⁶⁴.

The deposition process, including substrate temperature, substrate bias voltage, adatom mobility, and the ratio of ions to atoms incident on the substrate, plays crucial roles in film growth and microstructure development. It's worth noting that all these parameters directly impact the energy delivered to the growing film. Therefore, energy is the critical factor in adatom diffusion and, consequently, the final coating microstructure. This understanding is fundamental in our exploration of thin film deposition and microstructure development¹⁷⁶.

Following nucleation, the growth of the film can be defined by a structure zone model (SZM). The first model of SZM was proposed by Movchan and Demchishin for vacuum-deposited coatings in 1969 (Figure 39). This model is based on the ratio of the substrate temperature (T_s) and the melting point of the coating material (T_m), growing evaporated films of thickness between 0,3 to 2 mm. They described three types of growing zones with different structural and physical characteristics.

First, zone I, where the grain mobility is low, causes frequent nucleation of grains. Consequently, a columnar structure is formed and identified with inverted cone-shaped units and grains separated by pores. Secondly, in zone II, the temperature increases and although the structure still has a columnar shape, the voids between the columns are extinct. Thirdly, with a further rise in the temperature in zone III, a recrystallization and grain growth process develop, creating "fully dense" structures, more like the bulk material¹⁷⁷.



Figure 39 – Structure zone model proposed by Movchan and Demchishin¹⁷⁷.

Then, in 1974, a SZM model was proposed by Thornton considering sputtered films, once several investigations have demonstrated the significant influence of ion bombardment in the structure and consequently on the film's properties^{178,179}. The Thornton model is founded on films from 20 to 250 μ m of Ti, Cr, Fe, Cu, Mo, and Al coatings. In addition to the ratio T_s/T_m, his model also considered the argon sputtering gas pressure.

According to this theory, the film growth presented one more zone, additionally to the other three, the zone T (Figure 40). The zone I can evolve at low temperatures and high pressure due to the gas-phase scattering. The films created at this stage can be amorphous or crystalline and can be characterised as columnar shapes with elevated surface areas. Zone T is now present as a transition between zones I and II, presenting fibrous and dense-packed films. This structure is created at low gas pressures because of the energetic bombardment originating from high-energy neutrals from the sputtering target. Next, the structure turns columnar in zone II, but intercolumnar boundaries are denser than in zone I. This is due to the sufficient mobility of adatoms to diffuse. Finally, in zone III, the elevated surface temperature results in a higher grain boundary diffusion process, leading to the coating's recrystallisation, grain growth, and densification^{180,181}.



Figure 40 – SZM model introduced by Thornton considering sputtered films deposition¹⁸¹.

In 1998, Kelly and Arnell proposed the SZM model, considering a closed field unbalanced magnetron sputtering deposition configuration. Their model is based on the homologous temperature (T_s/T_m), bias voltage representing the ion energy, and the ion-to-atom ratio incident over the substrate representing the ion flux (J_i/J_a). Their findings demonstrated that voided and porous structures were extinct using this coating technology. Only fully dense (zone III) or dense columnar structures (zone II) were formed. As shown in Figure 41, this 3D model demonstrated that creating a dense microstructure at relatively low temperatures is possible, which expands the coating applications to temperature-sensitive substrates like polymers¹⁷⁶.



Figure 41 – SZM for unbalanced closed field magnetron sputtered films²¹.

II. Methodology

Chapter 3. Deposition process and experimental techniques.

3.1 Film deposition

The coatings were deposited using a pulsed DC magnetron sputtering system. This system was equipped with two unbalanced rectangular magnetron deposition heads, each measuring 300 x 100 mm, which were positioned on the roof of the chamber in a sputter-down configuration (as shown in Figure 42). A single chromium target with a purity of 99.5% was mounted on one of the magnetrons for the deposition process. The substrates were ZIRLOTM alloy coupons, sized 30 x 20 x 1 mm, which were ultrasonically pre-cleaned in acetone for 10 min prior to deposition. The substrates were placed on a sample holder below the magnetron, which was rotated during deposition to ensure uniform thickness of the Cr coatings. The magnetron was powered by an Advanced Energy Pinnacle Plus power supply in pulsed DC mode, operating at 100 kHz and 80% duty.



Figure 42 – Schematic representation of the sputtering rig.

The distance between the target and the substrate was maintained at 13 cm for all deposition runs. All the samples were sputter cleaned for 15 min at -650V before the deposition. The working pressure of the Cr-coated samples was 0.36 Pa. Samples were coated with no bias applied (NBA), i.e., at floating potential, followed by applied DC biases from -50V to -200V. After the deposition runs, the

substrates were allowed to cool down before the chamber was vented and the substrates removed.

Chromium nitride coatings

This project concentrated on producing stoichiometric CrN coatings, once it had been found in the literature that CrN coatings exhibited a denser microstructure and better wear results than Cr₂N coatings¹²¹. To achieve stoichiometric CrN coatings, a critical step is to determine the appropriate amount of nitrogen. In this research, we employ partial pressure control as a method to study the optimal N₂ flow rate, a key factor in achieving stoichiometric CrN coatings¹⁵⁶.

The total pressure of the system is determined by adding the partial pressures of each gas inside the chamber. Equation 4 represents the total pressure in the present study, where Pt is the total pressure, p_{Ar} is the argon partial pressure, and p_N is is the nitrogen partial pressure.

$P_t = p_{Ar} + p_N$ Equation 4

Therefore, the total and argon partial pressure are set to fixed values. Then, using a reactive feedback control system, the nitrogen flow is adjusted to maintain the total pressure fixed as determined. Thus, if nitrogen is in excess in the chamber, the system reduces the N_2 flow. Similarly, if nitrogen is consumed, the system increases the N_2 flow, resulting in a controlled ambient to produce a stoichiometric film.

This work fixed the Ar pressure at 1.4 mTorr (0.19 Pa). Then, the total pressure was fixed at 1.6 mTorr (0.21 Pa), 1.7 mTorr (0.23 Pa), 1.8 mTorr (0.24 Pa), and 1.9 mTorr (0.25 Pa) by adjusting the N₂ flow rates. Then, a composition study of Cr_xN was carried out using an EDX.

During deposition, an implemented capacitance manometer facilitates accurate pressure control. The pressure partial control recipes for the gas compositions (Ar/N2) study were set in a vacuum system controller (946 MKS Ltd.). Then, the gases were regulated using individual Horiba mass flow controllers (MFC) connected to the vacuum system controller.

The Cr_xN deposition parameters were the same as the Cr metallic coating. However, the bias voltage applied was only -50V for these samples.
3.2 Experimental techniques

Understanding the mechanical and tribological properties of chromium coatings is crucial for their application as an accident tolerant fuel. This topic will describe the techniques employed in this work: tribology friction tests, nanoindentation, and scratch tests.

3.2.1 Tribology test

The friction wear tests were conducted using a tribometer with a linear reciprocating movement to simulate the grid-to-rod phenomenon. Although a 'true' fretting module was not available for the tribometer, which requires an amplitude of less than approximately 100 μ m to accurately replicate fretting wear, the equipment used in this study had a minimum amplitude of 2 mm.

In this tribometer, friction occurs between the sample and a counter body, which is a pin holding a removable ball. The ball can be made of any desired material, allowing for flexibility in testing different material interactions. The pin is located perpendicular to the sample, as can be seen in Figure 43. During the experiment, the pin moves back and forth over the sample at a predetermined load and frequency. At the end of the experiment, a wear track is created on the sample surface.



Figure 43 – Image of the pin-on-disc tribometer.

It is important to note that although this equipment does not exactly replicate the GTRF phenomenon, it will be able to represent a simulation close to real movement. In addition, the samples were tested under the same fretting conditions, so the wear tracks in the samples will be comparable.

The experiments were carried out in an ambient environment using an Anton Paar Pin-on-Disc (TRB3) Tribometer with a 6 mm diameter AISI 316 stainless steel ball. Coatings were tested at three loads: 3, 4 and 5N, at a frequency of 10Hz with a full amplitude of 4 mm. The total distance was 50 m, accounting for 10 minutes tests. The tests were repeated three times for each sample and load used. The wear depths and wear volume were measured using a white light interferometer, Profilm3D. The wear tracks were also analysed in the SEM and EDX.

The specific wear rate (W_s) was calculated as defined¹⁸²: the wear volume of the material (V), divided by the applied normal load (N), and sliding distance (d), as detailed in Equation 5:

$$W_s = \frac{\Delta V}{Nd}$$
 Equation 5

The wear volume was estimated using Equation 6⁸:

$$V = Ad$$
 Equation 6

Where A indicates the cross-section worn area (μm^2) and d is the sliding distance (4mm).

3.2.2 Nanoindentation

Nanoindentation is a precise technique to measure the hardness and elastic modulus of coatings. In this method, a hard and sharp indenter made of diamond is pressed into the surface of the sample with a controlled load. Then, the equipment records the load and the depth of penetration to calculate the hardness and elastic modulus. In order to determine the material's mechanical properties, established models, such as Oliver-Pharr, are used to analyse the load-displacement data.

The coating hardness (H) was measured using a nano-indenter (Anton Paar – Nanoindentation tester: NHT³). The applied maximum load was 50 mN, and the loading rate was 33 nm.s⁻¹ for all measurements, which ensured that the maximum penetration depth was less than 10% of the film thickness. After indentation, the results were analysed using Oliver and Pharr's theory to obtain the hardness values.

In addition, the coating's toughness was qualitatively assessed by the induction of cracks using a Vickers hardness tester (Future-tech FV-310) equipped with a diamond indenter and applying loads of 30 kgf.

3.2.3 Scratch test

The scratch test is a method for evaluating the adhesion and mechanical properties of thin films. This technology involves dragging a diamond stylus (indenter) across the samples' surface with a controlled and gradually increasing load until the coating fails. The equipment has a precision instrument that records the applied force, stylus displacement, and acoustic emission during the scratching test. Failure points are identified at which the coating delaminates or fractures, revealing the coating's adhesion and mechanical resistance.

In this project, the scratch test was performed in a Micro Combi Tester (MCT³) from Anton Paar. The normal load applied to the coating gradually increased from 0 N to 30 N at a rate of 40 N/min, and the length of the scratch was 3 mm. The normal load, acoustic signal, and penetration depth were obtained and recorded by the tester during scratch testing.

Chapter 4. Analytical techniques

This chapter details the analytical techniques employed to examine the chromium-based coatings discussed in this thesis. It includes background information and an assessment of the applicability of these analytical techniques to the current research project.

4.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) is a non-destructive analytical technique used to determine the crystal phases existing in materials. The technique can also be used to measure characteristics of materials such as grain size, preferred orientation, and phase composition.

X-rays are generated from electromagnetic radiation and have high energies and short wavelengths, in the Ångstrom (10⁻¹⁰ m) range, which is the same order of magnitude as the atomic spacing of solids. When the X-rays are emitted in the sample's direction, they penetrate the material and part of the beam is scattered in all directions by the electrons associated with each atom. The diffracted beam direction depends on the planes in the crystalline solid. The diffracted beam is detected and measured, typically by a detector that moves around the sample. By analysing diffraction patterns, which consist of peaks at specific angles, crystal structure and other properties of samples can be determined¹⁸³.

The Braggs law equation is used to calculate the value of the crystal lattice spacing, d using the diffracted angle, showed in Equation 7. Bragg diffraction occurs when radiation with a wavelength, λ is reflected like a mirror by atomic planes in a crystal, leading to constructive interference.

$n\lambda = 2d \times \sin \theta$ Equation 7

Where n is the order of reflection, which could be any integer (1, 2, 3, ...), λ is the wavelength of the X-ray beam, d is the crystal lattice spacing, and θ is a diffraction angle. The schematic illustration of the technique and Braggs law diffraction is demonstrated in Figure 43.



Figure 44 – Schematic illustration of diffraction of X-rays by planes of atoms¹⁸³.

In XRD analysis, there is also a mode called grazing incidence that employs a small incidence angle for the X-rays hitting the material, which limits the penetration depth into the material. By minimizing the penetration depth, this mode reduces the interference from underlying substrates, providing more accurate results and a more suitable technique for thin films.

Identifying phases is one of the primary applications of XRD techniques in analysing thin films. By comparing the XRD patterns of unknown samples with the standard patterns in the Powder Diffraction File (PDF) database, it is possible to accurately determine the phases present in the sample.

In this work, the crystallinity of the thin films was assessed by X-ray diffraction (XRD), on a Bruker D8 advanced system. CuK α radiation at 0.154 nm was used, in grazing incidence mode at 3°, over a scan range from 10 to 100° 2 θ . The accelerating voltage and applied current were set to 40 kV and 40 mA, respectively.

4.2 Electron microscopy

4.2.1 Scanning electron microscopy (SEM)

A scanning electron microscopy (SEM) is a versatile, non-destructive tool frequently used to examine and analyse the surface morphology and composition

of various materials. It offers spatial resolution down to 1 nm. By scanning a focused electron beam across a sample, the composition, topography, and other properties can be determined.

The analysis starts with forming primary electrons using an electron gun and electromagnetic lenses to focus the electron beam. The acceleration voltage can reach up to 30 kV, and the operation is conducted under a vacuum to avoid collisions between primary electrons and gas particles. Then, the electron beam interacts with the material's atoms and produces secondary electrons, backscattered electrons and characteristic X-rays, illustrated in Figure 45. The signals formed during the interaction are collected and processed by a computer to create images or obtain information from the sample¹⁸⁴.



Figure 45 – Schematic illustration of emitted signals of electron beam interaction with the sample.

The secondary electrons are formed due to an inelastic collision between the primary electrons and atoms from the sample surface. It provides detailed images of a sample that are ideal for the study of its morphology and topography. Meanwhile, backscattered electrons are generated by the inelastic collision between the emitted electrons beam and the nucleus of the surface sample. Inelastic collisions happen more often in heavy elements than in light ones. Thus, the areas composed of heavy elements appear brighter than lighter elements in

the image. It helps identify multiple phases or obtain high-resolution compositional maps¹⁸⁴.

In order to avoid electrostatic charging effects, samples should be electrically conductive; alternatively, they should be coated with a thin conductive layer (Au, Pt, etc.) using a diode DC sputtering process.

4.2.1.1 Energy dispersive X-ray spectroscopy (EDX)

Energy dispersive X-ray spectrometry is a chemical microanalysis technique used in conjunction with SEM.

When the high-energy electrons from the electron beam interact with the sample surface, they can eject electrons, creating a positively charged hole. This hole is then filled by an electron from a higher energy shell, releasing excess energy as characteristic X-rays. The energy of these X-rays is directly related to the atomic number of the element, allowing for precise element identification¹⁸⁴.

EDX also enables qualitative analysis. The concentration of each element is determined by measuring the line intensities and comparing them with calibration samples that contain known compositions of the same elements, providing a reliable method for element identification¹⁸⁴.

In this work, the morphology and composition of the thin film produced were carried out in three different SEM equipment. The high-magnification images were first performed in a Zeiss Supra 40 VP-FEG-SEM. Then, due to an equipment renovation, the final images were evaluated by a Zeiss Crossbeam 350 FIB-SEM. The composition was determined by EDX systems installed on the mentioned microscopes.

The low-magnification images of the worn surfaces were performed in a Hitachi TM4000Plus Tabletop SEM. The composition of the wear track was also analysed using EDX installed in this equipment.

4.2.2 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a technique for assessing a sample's refined details at the atomic or molecular level. TEM can offer high-

resolution images and information about the internal structure, composition, morphology, structural properties, and grain size.

In operation, an electron gun meticulously generates and accelerates an electron beam towards the sample. This beam, upon passing through the sample, interacts with the electrons of the sample's atoms. The resulting image is a product of the information collected from the excited electron waves. These waves are then distributed to the image recording section by an objective lens. The complexity of TEM operation is further highlighted by the fact that higher resolution images can be obtained by using incident electrons with higher energies and thinner samples, as the intensity of the image is proportional to the time-averaged amplitude of the electron wavefunctions¹⁸⁴.

The acceleration voltage varies from 60 to 300 kV, and the analysis is conducted under ultra-high vacuum to prevent electron beam interference from gas particles. TEM images provide a 2D projection of the sample's inner structure¹⁸⁴.

In this project, TEM (STEM) images were acquired using a TESCAN Tensor microscope operated at an accelerating voltage of 100 kV.

4.3 Atomic force microscopy (AFM)

Scanning probe microscopy (SPM) is a versatile, non-destructive, and highresolution technique that is exceptionally effective for examining the morphology and specific properties of solid material surfaces. SPM has been fundamental in advancing studies and developing new methodologies in surface engineering and nanotechnology. SPM encompasses a variety of techniques, each employing a tip that interacts differently with the material's surface. These interactions, which define each specific SPM technique, can involve phenomena such as quantum tunnelling (as in scanning tunnelling microscopy, STM), magnetic forces (as in magnetic force microscopy, MFM), and electric forces (as in electric force microscopy, EFM)¹⁸⁵.

One notable category within SPM is atomic force microscopy (AFM), where the tip interacts with the sample surface through atomic forces, such as van der Waals interactions. As detailed in Figure 46, AFM utilizes a sharp probe with a fixed flexible cantilever that scans the sample surface; when the probe moves over

the surface, it interacts with the atoms. This interaction leads to a deflection in the cantilever, measured by a laser beam sensitive to movement and identified in a detector. Then, the deflection is converted into topographical data, generating 3D surface profiles at the nanometre scale and information about the surface, such as roughness and surface area¹⁸⁵.



Figure 46 – Schematic illustration of AFM probe¹⁸⁵.

AFM instruments offer three distinct imaging modes: contact, tapping, and non-contact. Each mode has its unique characteristics and is suited for different types of samples¹⁸⁵.

In the contact mode, the cantilevered force sensor is in continuous physical contact with the sample during the scanning. Although this mode provides high-resolution images, it could lead to tip wear and damage and potentially damage soft samples. It is suitable for samples with hard surfaces.

In tapping mode, the cantilever only periodically contacts the sample surface at its resonant frequency or near it. As a result, high-resolution images are acquired while minimizing damage to the sample by lateral forces. It is ideal for soft, sticky, or delicate samples such as biological specimens and polymers.

In the non-contact mode, the cantilever oscillates at its resonant frequency, and the tip stays just above the surface, detecting attractive forces. This mode provides a lower resolution than the other two modes; however, the probe tip and sample damage are minimized. It is also recommended for very soft and adhesive samples. This work performed AFM analysis on a Horiba XPlora Plus atomic force microscopy (AFM) system in non-contact mode.

4.4 Optical profilometry

White light interferometry (WLI) is an optical measurement method to scanning a sample topography with high precision and non-contact. It uses the white light broad spectrum of wavelengths to create detailed 3D images of surfaces.

The WLI uses a white light source split into two beams, one beam is directed to a reference mirror and the other beam is pointed to the sample surface. The beams are reflected and recombined to form an interference pattern. Reference and sample beams have different optical path lengths, which determines the pattern. Then, the sample is scanned, and at each step an interference pattern is recorded. Finally, the interference patterns are processed and determine a point at which the optical path lengths match, thus the points are connected to the surface height at each pixel, forming a 3D map of the surface¹⁸⁶. The illustration of a white light interferometry is presented in Figure 47.



Figure 47 – Illustration of white light profilometry.

The average roughness (Ra) and surface images of the worn coated surfaces were performed in a white light interferometer, Profilm3D from Filmetrics, with a magnification of 50x.

The roughness was measured through the arithmetic mean of the absolute values of the ordinates of the roughness profile, called Ra. The roughness was measured perpendicularly to the sample scratches in three random areas of each sample.

4.5 Contact Angle Goniometry

Contact goniometry is the equipment used to define the wettability of the samples' surfaces. It measures the contact angle between a fluid drop and a solid surface. In practice, a droplet of water is deposited using a syringe over the sample's surface. Then, a camera captures images of this drop resting over the surface. The contact is calculated by analysing the captured image, which is the angle formed at the intersection of liquid-solid and liquid-air interfaces¹⁸⁷.

Depending on the contact angle, the material can be classified as hydrophobic when the contact angle is higher than 90° or hydrophilic when the contact angle is lower than 90°¹⁸⁷. A schematic illustration of the contact angle for both hydrophobic and hydrophilic modes are presented in Figure 48.



Figure 48 – Schematic illustration of the contact angle for both hydrophobic and hydrophilic modes.

In this project, the software measured the drop base diameter at room temperature by capturing the spreading of around 5 μ L of a DI water droplet with a recording rate of 10 frames/s.

III. Results and discussion

Chapter 5. Chromium coating: Roughness and wettability

In the Chapter 6 we aim to explore and to establish the influence of the surface roughness on the wettability of the chromium coatings and the substrate.

5.1 Coating overview

The characteristics of the coating's surface can affect the critical heat flux of the claddings, it can delay the boiling crisis or improve boiling efficiency. There is a direct relationship between surface wettability and nucleation site, bubble density, and bubble departure diameter. It is known that surface roughness can significantly influence the wettability of surfaces¹⁸⁸. Therefore, it is essential to study the roughness and its influence in the contact angle of a coating deposited on the zirconium cladding.

Research has demonstrated that increased surface wettability (contact angle θ < 90°) results in a reduced bubble departure frequency. In other words, a smaller contact angle indicates higher wettability, which consequently leads to an increase in the critical heat flux (CHF). Therefore, a new ATF should possess a contact angle that is similar to or lower than that of the zirconium alloys currently in use. This ensures the ATF material maintains or improves upon the wettability characteristics essential for optimal performance under high-heat conditions⁵⁸.

To understand the effect of the roughness of Cr coatings, the Zr-2 substrates were mechanically polished using abrasive paper with different mesh numbers: 240, 400, 2500 grit, and 1 μ m. Then, two samples of each polished substrate were coated for 4 hours using -50 and -100V bias voltages. The roughness and contact angle measurements were performed five times in random areas of each sample.

The information on the sample's identification according to the polishing and bias voltage used is presented in Table 2.

Coating	Bias (V)	Polishing mesh	Sample ID	Thickness (mm)
Uncoated	-	240 grit	Zr_240	-
	-	400 grit	Zr_400	-
	-	2500 grit	Zr_2500	-
	-	1 µm	Zr_1µm	-
Cr	-50V	240 grit	Cr_50_240	4.25 ± 0.04
	-50V	400 grit	Cr_50_400	4.57 ± 0.01
	-50V	2500 grit	Cr_50_2500	4.80 ± 0.04
	-50V	1 μm	Cr_50_1µm	4.84 ± 0.03
Cr	-100V	240 grit	Cr_100_240	3.92 ± 0.17
	-100V	400 grit	Cr_100_400	4.08 ± 0.35
	-100V	2500 grit	Cr_100_2500	4.28 ± 0.12
	-100V	1 μm	Cr_100_1µm	4.28 ± 0.01

Table 2 – Sample's identification according to the polishing and biasvoltage.

5.2 Coating morphology

Figure 49 and Figure 50 present the top surface SEM images of selected coatings. As can be seen in the images, the surface morphology differs significantly in shape on the bias voltage used.



Figure 49 – SEM top surface images of chromium coatings deposited at - 50V bias on Zr-2 substrates polished at 240, 400, 2500 grit, and 1 μ m.



Figure 50 – SEM top surface images of chromium coatings deposited at - 100V bias on Zr-2 substrates polished at 240, 400, 2500 grit, and 1 μ m.

Figure 51 and Figure 52 represent the fracture-section images of each deposition. These samples were deposited on silicon wafers, which were fractured to assess the SEM cross-section images.



Figure 51 – SEM cross-section images of chromium coatings deposited at - 50V bias on Zr-2 substrates polished at 240, 400, 2500 grit, and 1 μ m.



Figure 52 – SEM cross-section images of chromium coatings deposited at - 100V bias on Zr-2 substrates polished at 240, 400, 2500 grit, and 1 μ m.

The surface morphology of the -50V bias voltage samples (Figure 49) shows a densely packed structure, with the grain boundaries clearly visible. When the voltage is increased to -100V (Figure 50) the surface became visually smoother. The grains look densely packed, but it seems a more interconnected microstructure. As a result of high-energy ion bombardment, highly mobile adatoms diffuse into the inter-grain voids, increasing the density and compactness of the film. Also, particle distribution becomes more uniform over the surface, decreasing the tendency for columnar growth^{189,190}.

Regarding the cross-section images, both films coated with -50V (Figure 51) and -100V (Figure 52) bias voltages demonstrated dense and columnar structures. Although the surface morphology differs from -50V and -100V bias, these coatings' cross-sections look similar. In each group of bias voltage used, the different substrate roughness does not seem to show differences in the coatings' morphology.

5.3 XRD results

Figure 53 and Figure 54 give the X-ray patterns of the Cr-coated samples at -50V and -100V, respectively.



Polished samples (-50V)

Figure 53 – XRD patterns of chromium coatings deposited at -50V bias on Zr-2 substrates polished at 240, 400, 2500 grit, and 1 μ m.

Polished samples (-100V)



Figure 54 – XRD patterns of chromium coatings deposited at -100V bias on Zr-2 substrates polished at 240, 400, 2500 grit, and 1 μ m.

All the films presented a high-intensity peak at around $2\theta = 44.3^{\circ}$, corresponding to the (110) Cr peak, and two low-intensity peaks corresponding to the (200) and (211) planes at about $2\theta = 64.5^{\circ}$ and 81.7° (PDF card, 85-1336).

In general, all the coatings presented a strong (110) texture. Gautier *et al.* investigation discuss the effects of some deposition parameters on the texture of chromium films using vacuum arc evaporation¹⁹¹. They discuss that PVD coatings often exhibit a preferred crystallographic orientation. They explain that under specific conditions—such as substrate temperature, deposition rate, or film thickness—the coating tends to align with the crystallographic planes that have the highest reticular density. For pure chromium, the (110) plane is expected to be the preferred orientation due to its highest reticular density of 1.414 atoms/a². In contrast, the other observed planes have lower densities, with the (200) plane at 1 atom/a² and the (211) plane at 0.81 atoms/a². The findings in this work appear to be consistent with these predictions.

Table 3 shows the absolute and relative intensities of the (110) diffraction plane. The peak intensity ratio I(200) / I(110) can be used as an indicator to evaluate the crystallographic orientation of the Cr coatings deposited under different conditions. According to the literature for chromium, the (110), (200) and

(211) peaks in Cr powder have relative intensities of 100%, 29% and 16%, respectively.

Gautier *et al.* study also claim that only two parameters seem to significantly affect the texture of the coatings: the substrate temperature and the bias voltage. They argue that during deposition, impurities originating from the outgassing of chamber walls or from the target itself can become incorporated into the coating. These impurities hinder the growth of the (110) plane. However, when bias voltage is applied, these impurities are sputtered away from the surface, allowing the (110) texture to develop more freely¹⁹¹. Therefore, based on their prediction, bias voltage promotes (110) texture.

	XRD absolute intensity (counts)		Relative intensity to (110) plane (%)			
Plane	110	200	211	110	200	211
Cr (Ref.) ¹⁹²	-	-	-	100	29	16
Cr_50_240	20857	3163	2547	100	15	12
Cr_50_400	22968	2893	2560	100	13	11
Cr_50_2500	14014	1734	1350	100	12	10
Cr_50_1µm	16244	2405	2102	100	15	13
Cr_100_240	16884	2463	2009	100	15	12
Cr_100_400	21282	3184	2554	100	15	12
Cr_100_2500	18987	3322	2992	100	17	16
Cr_100_1µm	14346	2504	2127	100	17	15

Table 3 – Experimental results: XRD absolute intensity and XRD relativeintensity to (110) diffraction plane for all the Cr-coatedsamples with polished substrates.

All the results of the Cr coatings in Table 3 confirms a pronounced (110) preferential orientation, with the (200) and (211) ratios remaining lower than the reference. In addition, comparing the relative peak heights for the (110), (200) and (211), it can be inferred that the textures of Cr coatings were not significantly affected for the different substrate roughness.

5.4 Surface roughness and contact angle.

Figure 55 presents the WLT images of the polished substrate with different mesh numbers: 240, 400, 2500 grit, and 1 μ m. Figure 56 and Figure 57 show the WLI images of the Cr-coating on the polished substrates at -50V and -100V bias voltage, respectively. The average roughness (Ra) values for these samples are provided in the images.



Figure 55 – WLI images of Zr-2 polished at 240, 400, 2500 grit, and 1 μ m.



Figure 56 – WLI images of chromium coatings deposited at -50V bias on Zr-2 substrates polished at 240, 400, 2500 grit, and 1 μ m.



Figure 57 – WLI images of chromium coatings deposited at -100V bias on Zr-2 substrates polished at 240, 400, 2500 grit, and 1 μ m.

As can be seen in Figure 55, the surface roughness differences for the substrates are clearly visible, and the roughness values gradually decrease with the increase of the grit sizes, as expected. The substrate polished with 240 grit presented prominent peaks and valleys; also, the surface exhibited a significant number of scratches. Consequently, these samples presented the highest roughness average value, Ra, of 20 μ m. In the sequence, the surfaces polished at 400 grit appear more uniform than those at 240 grit, with reduced peak-to-valley height variations. This results in a drop in Ra from 0.20 to 0.12 μ m. Next, the substrates are polished until 2500 grit, presenting a smoother surface (Ra = 0.12 μ m) with lower variations and a more uniform texture. The Zr_1 μ m samples demonstrated a significantly smoother surface, achieving a highly polished texture with 0.02 μ m average roughness.

Figure 56 and Figure 57 present the WLI images of the Cr-coated substrates onto the different roughness substrates using -50V and -100V bias voltage, respectively. The coating morphology and roughness closely mirror those of uncoated polished substrates, providing strong evidence that the coating was deposited in accordance with the substrate roughness, i.e., the coating is conformal.

Figure 58 displays the contact angle images of the substrate surface and both sets of Cr-coatings at -50V and -100V onto the polished substrates. The average contact angle values for these samples are shown in the images. In addition, Table 4 and Figure 59 sums up the contact angle and roughness for the same samples.



Figure 58 – Photographs illustrating the contact angle for (a)–(d) uncoated Zr-2; (e)–(h) Cr-coated Zr-2 at -50V; and (i)–(l) Cr-coated Zr-2 at -100V, with each substrate polished at 240, 400, 2500 grit, and 1 μm.

Table 4 – Contact angles and roughness results of the uncoated substrate and Cr-coated Zr-2 with -50V and -100V bias and polished at 240, 400, 2500 grit, and 1 μ m.

Sample ID	Contact angle (°)	Ra (μm)
Zr_240	61.6 ± 8.3	0.20 ± 0.04
Zr_400	66.5 ± 7.8	0.12 ± 0.03
Zr_2500	73.4 ± 2.2	0.10 ± 0.03
Zr_1µm	85.9 ± 1.8	0.02 ± 0.01
Cr_50_240	108.2 ± 1.94	0.17 ± 0.05
Cr_50_400	107.2 ± 1.64	0.12 ± 0.02
Cr_50_2500	105.5 ± 2.58	0.10 ± 0.02
Cr_50_1µm	104.0 ± 1.35	0.02 ± 0.01
Cr_100_240	103.5 ± 0.95	0.21 ± 0.06
Cr_100_400	105.1 ± 1.58	0.14 ± 0.03
Cr_100_2500	104.7 ± 1.41	0.11 ± 0.02
Cr_100_1µm	105.1 ± 2.35	0.04 ± 0.01



Figure 59 – Graph of contact angles and roughness results of the uncoated substrate and Cr-coated Zr-2 with -50V and -100V bias and polished at 240, 400, 2500 grit, and 1 μ m.

As illustrated in Figure 58 and listed in Table 4, the uncoated substrates presented a hydrophilic behaviour ($\theta < 90^{\circ}$). In addition, the contact angle increases with the decrease of the substrate roughness. The rougher sample surface Zr_240 presented the lowest contact angle of about 61°, then the contact angle gradually increased, achieving a value around 86° for the smoother surface on the sample Zr_1µm. In other words, the surface became less hydrophobic, which is not ideal to improve the cladding performance.

However, after the polished substrates were coated with chromium, the surface became hydrophobic ($\theta > 90^{\circ}$). This result unexpectedly contradicts the goals for developing a new ATF design. Increasing, or at least maintaining, the hydrophilicity of the zirconium substrate would be ideal for this application. A lower contact angle, indicating a more hydrophilic material, would increase the critical heat flux (CHF) performance, since CHF generally increases with decreasing contact angle. This improvement would occur because a more hydrophilic surface reduces the bubble outflow frequency, thus increasing CHF⁵⁸.

Furthermore, the samples exhibited a decrease in surface roughness even after the deposition of Cr coatings onto the polished substrates. However, the contact angle measurements did not show significant variations. As illustrated in Figure 59, a slight decrease in contact angle was observed for the samples coated at a bias voltage of -50 V. Nevertheless, this reduction was not substantial and did not alter the inherent hydrophobic behaviour of the chromium coatings. Overall, the contact angles remained consistent across all samples—approximately 105°—regardless of the surface roughness or the applied bias voltage (-50 V or -100 V).

In Table 5, we present a comparison of the contact angle for Cr coatings reported in other works. This table also includes results from a comprehensive report edited by MIT and Idaho National Lab (INL)¹⁹³, which compiled data on the wettability of ATF cladding materials in collaboration with various universities and industrial partners. The results of Cr-coatings developed by two different universities shown in this report are displayed in Table 5.

Author/	Deposition	Cubatrata	Contact	De	
University	process	Substrate	angle	Ra	
Lee et al. ¹⁹⁴	PVD	Zr-4	88.37	0.16	
	Cold spray	Zr-4	93.98	0.53	
	Magnetron	high alloyed steel	00 30	0.19	
	sputtering	X155CrVMo12-1	33.30		
Krum <i>et al.</i> ¹⁹⁵	Magnetron	high alloyed steel			
	magnetion	X155CrVMo12-1	47.50	0.027	
	sputtering	(Polished: 2500 grit)			
Kam et al ¹⁹⁶	Electroplating	Stainless steel	80	0.024	
		Zr-4	20.51	0.442	
Virginia		(as received)	20.01		
Commonwealth	חעם	Zr-4	20.02	0.498	
University	FVD	(Polished: 600 grit)	29.03		
(VCU) ¹⁹³		Zr-4	20.64	0.910	
		(Polished: 240 grit)	29.04		
University of					
Wisconsin at	Spray coated	Zirlo	77	0.07	
Madison	Opray-coaled	ZIIIO			
(UWM) ¹⁹³					

Table 5 - Summary of previous contact angle measurement on Cr-coatedsurfaces

As can be seen in Table 5, there is no clear relationship between wettability and roughness on Cr-coated surfaces according to the literature. For instance, Lee *et al.* noticed a drastic roughness difference between PVD and cold spray, 0.16 and 0.54 μ m. However, they observed a small difference in the contact angle, only about 5° higher for cold spray deposition. These results demonstrated that despite the very different roughness between the samples, other factors influence the wettability results, such as the deposition process in this case.

On the other hand, Krum *et al.* used the same deposition technique but polished only one of the substrates before the coating. The polished Cr-coated

substrate presented a roughness of 0.027 μ m, while the unpolished Cr-coated substrate showed 0.19 μ m. However, the smoother sample demonstrated a significantly lower contact angle than the rougher one, from 99° to 47°.

Another interesting result was observed in the Virginia Commonwealth University (VCU) study. In their investigation, the substrates were previously polished with different grits, 600 and 240 grit. Then, the samples presented very different roughness, around 0.5 and 0.9 μ m, respectively. However, similarly to this work, both presented almost the same contact angle values, about 29°. Despite the significant differences in contact angle findings, it seems that roughness is not the main factor influencing the contact angle in some cases.

Overall, most of the Cr coatings previously reported showed a hydrophilic profile, while in the present work, they presented a hydrophobic profile. However, there is no clear concordance in the values reported by other studies.

Moreover, this work observed that when the surface became hydrophobic, the roughness stopped influencing the contact angle. Therefore, the reasons for this behaviour will be discussed below.

Wenzel's model describes the effect of roughness on contact angle¹⁹⁷. Wenzel's theory says that when a water droplet reaches a rough surface, the drop wets the surface thoroughly, as illustrated in Figure 60(a). According to his model, surface roughness decreases the contact angle of a droplet on a hydrophilic surface while increasing the contact angle on a hydrophobic surface. The reason for the drop in the contact angle is related to droplet spreading along the grooves^{188,198}.

The situation becomes more complex when the contact angle lies between 90° and 180°. Under these circumstances, the drop does not penetrate the surface grooves because asperity valleys can trap gas molecules. Cassie and Baxter proposed a model for this circumstance, which can be applied to rough surfaces that can trap air in the groove asperities Figure 60(b). Due to this, liquid-solid interfaces are not continuous and solid-liquid interfaces alternate with gas-liquid interfaces¹⁹⁹.



Figure 60 – A schematic illustration of the difference between (a) Wenzel and (b)Cassie–Baxter wetting regimes.

The basic idea behind both models is that they minimize the absolute change in surface energy resulting from solid-liquid, solid-air, and water-air interfaces. Small drops of water on surfaces can be understood as forms of equilibrium that minimize changes in surface energy. Combining these two theories and a surface roughness analysis can provide a comprehensive and accurate explanation of actual manufactured rough surfaces¹⁸⁸.

In this work, Wendel's relation could be noticed in the zirconium-based substrate, as it shows a hydrophilic profile, and the contact angle decreases with the roughness increase. However, when the samples are Cr-coated, the surface changes for a hydrophobic behaviour and no longer obeys Wendel's relation. The presence of chromium causes a shift to the Cassie Baxter wettability mode.

Krum *et al.* also observed the exact change for the Cr-coated rougher surface. They related the Cassio Baxter change mode to two possible reasons. First is the shape and distribution of crystal tips, and second is step-like nano/micro morphology along the surface¹⁹⁵. Therefore, although the chromium surface usually presents a relatively high surface energy, its surface probably offers a convenient surface topography propitious to hydrophobic behaviour in Cassie Baxter's state.

Another consideration is that although surface roughness is recognized as a factor that significantly influences the contact angle, there are many other factors that influence real surface wettability. These factors may include surface energy, chemical composition, heterogeneity, surface treatment, surface morphology and surface temperature and oxidation. Any of these other factors could prevail over the effect of roughness, resulting in a stable roughness regardless the substrate roughness differences.

For example, several studies have determined that the coating surface's chemical composition also affects its wettability^{200–202}. According to Dolique *et al.*,

high contact angles in AlCoCrCuFeNi alloy films are associated with higher Al and Cr contents²⁰³.

5.5 Summary

In this chapter, we aimed to understand the influence of substrate roughness on Cr-coating wettability. Additionally, we sought to manipulate the contact angle through roughness modification. To that end, we polished the Zr-2 substrate with four different abrasive papers with different grit sizes, which presented four different roughness to be tested.

We also investigated the influence of substrate bias on roughness by depositing coatings at -50V and -100V bias. Both presented a dense surface, but -50V bias showed more grain boundary edges. On the other hand, due to highenergy ion bombardment, the -100V bias coating surface became visually smoother with an interconnected microstructure. Concerning the coatings' crosssections, the morphology is alike, with dense columnar structures. The XRD patterns showed peak intensities for the (110), (200), and (211) planes for all the Cr coatings, but the (110) peak was the preferential texture in all cases.

Moreover, the results of our study revealed a clear and logical progression for the polished substrates. As the roughness of the uncoated Zr-2 substrate decreased, the contact angle increased, leading to a less hydrophilic behaviour.

Regarding the Cr-coated substrates, we noticed that the coating surface preserved the substrate's polished roughness even after deposition. However, we observed that the surface roughness did not affect the contact angle of the chromium coating in this case. Therefore, considering the deposition technique and parameters used in this work, the contact angle of the Cr-coated samples could not be manipulated by roughness.

We suspect that the chromium coating modifies the surface characteristics favourable to a shift towards the hydrophobic behaviour. Additionally, other factors that influence the wettability, such as surface energy, chemical composition, heterogeneity, surface treatment, etc., may prevail over the effect of roughness.

These findings suggests that the material, deposition technique or parameters tested in this study may not be ideal for improving CHF performance.

Additionally, decreasing the Zr-2 cladding roughness is not recommended either for this purpose.

Chapter 6. Influence of bias voltage on deposition rate and wear resistance of chromium coatings

The Chapter 7 focuses on a comprehensive study about the bias voltage influence in the deposition rate, structure morphology, and the friction wear on a thin chromium layer with a thickness of approximately 1 μ m or less.

6.1 Coating overview

The bias voltage is a parameter of high interest in producing denser structures. Previous studies reported the effects of different bias values on the chromium coating structure^{22,152,204}. Therefore, it is crucial to understand what and how these effects affect the Cr-coated cladding performance. The appropriate bias value is an important parameter to define in each case, as insufficient bias voltage may not provide the required density for substrate protection. Likewise, excessive biasing can result in high film stresses, with possible cracking and delamination of the film.

At the outset of this study, our primary objective was to determine the deposition rate and morphology of chromium (Cr) coatings on ZIRLO[™] substrates. The samples were ultrasonically pre-cleaned in acetone for 10 minutes before deposition. Subsequently, the samples underwent sputter cleaning for 15 minutes using a power of 100W and a substrate bias of -650V. Following this preparation, the substrates were coated with chromium for one hour. During this process, the following bias voltages were applied: -50V, -75V, -100V, -125V, -200V, and -250V.

In a subsequent stage of this study, we conducted a friction test to gain insights into the initial behaviour of the wear resistance of Cr-coatings under different bias voltages. The friction wear experiments were performed in a dry environment, using a 6 mm diameter AISI 316 stainless steel ball with a load of 1N. A frequency of 10Hz was used to create a linear wear track with a full amplitude of 4 mm. Three tests were conducted on each sample to calculate the average depth and wear area. The total distance covered was 50 m, accounting for 10 minutes of testing. The samples used included uncoated ZIRLO[™] and Cr-coated samples.

6.2 Coating morphology

Table 6 presents information on the sample's identification, thickness, and deposition rate (Dep. rate) according to the bias voltage used.

Sample ID	Bias (V)	Dep. rate (µm/h)	Thickness (μm)
50V_1h	-50	1.2	1.2 ± 0.04
75V_1h	-75	1.1	1.2 ± 0.03
100V_1h	-100	1.0	1.0 ± 0.03
125V_1h	-125	1.3	1.3 ± 0.03
150V_1h	-150	0.8	0.8 ± 0.07
200V_1h	-200	0.5	0.5 ± 0.02
250V_1h	-250	0.6	0.6 ± 0.01

 Table 6 - Sample's information according to bias voltage.

Figure 59 and Figure 60 present SEM images of the cross-section and top surface of the Cr coatings for bias testing.



Figure 61 – SEM cross-section and thickness of the chromium deposited at (a) -50V, (b)-75V, (c)-100V, (d)-125V, (e) -150, (f)-200, and -250V bias.
Varying the bias voltage produced differences in coating structure. As seen in the cross-section images in Figure 61, all the samples exhibited a packed and dense columnar structure. Additionally, the deposition rate gradually decreased during the bias voltage rise, resulting in a thinner coating at high voltage once the coating time was kept the same.

Sample 125V_1h, which presented the highest deposition rate value, showed an unexpected result. The sample's positioning on the substrate holder may vary slightly, which can result in a minor increase in the deposition rate. In addition, the unexpected result falls within the range of standard variation, indicating that it may still be valid despite initial surprises.

The logical connection between the deposition rate and the increasing bias voltage is clear. As the energy of the ions arriving at the substrate increases, it promotes knock-on implantation. This process, where energetic ions transfer enough energy to the film's atoms, embedding them beneath the film's surface, results in a decrease in apparent deposition rate. Therefore, the surface atoms are accommodated deeper into the structure, creating denser and thinner coatings. Furthermore, as the ions transfer more energy to adatoms, a considerable number of atoms can be re-sputtered from the surface, leading to a thinning of the thickness^{23,152,153,189}.



Figure 62 – SEM top surface images of chromium coatings deposited at (a) -50V, (b)-75V, (c)-100V, (d)-125V, (e) -150, (f)-200, and -250V bias.

Table 7 and Figure 62 displays the roughness values obtained from the WLI for the uncoated substrate ZIRLO and the Cr-coated samples from -50V to -250V.

Sample ID	Ra (µm)
ZIRLO™	0.12 ± 0.01
50V_1h	0.11 ± 0.02
75V_1h	0.11 ± 0.01
100V_1h	0.10 ± 0.03
125V_1h	0.11 ± 0.03
150V_1h	0.07 ± 0.01
200V_1h	0.08 ± 0.01
250V_1h	0.10 ± 0.20

 Table 7 – Roughness results of the uncoated substrate and Cr-coated samples

 from -50V to -250V bias voltage.



Figure 63 – Chart of the roughness results of the uncoated substrate and Crcoated samples from -50V to -250V bias voltage.

Figure 62 shows how the surface morphology differs significantly in shape on the bias voltage. The -50V bias sample exhibits a compact, continuous surface, and no apparent defects in sight. A significant change is observed in the -75V and -100V samples; the surface looks compact and continuous but smoother than the other samples. However, from bias voltages of -125V to -250V, there is a change in the surface shape. From -125V onwards, a gradual growth of particles on the surface with well-defined crystal boundaries between the particles is observed. These results might be a consequence of the high energy of the ion bombardment that leads to a higher mobility of the atoms on the surface. Then, small grains merge, resulting in a larger grain size^{189,190}.

However, even with the significant changes in the surface generated by the different bias voltages, there was not a drastic effect on the surface roughness, as can be seen in Table 7 and Figure 63. Even compared with the bare substrate, the coating's roughness presents similar values.

6.3 XRD results

Figure 64 present the X-ray patterns of the Cr-coated samples from -50V to - 250V bias voltage.



Figure 64 – XRD patterns of Cr-coated samples from -50V to -250V bias voltage.

Figure 64 shows that three prominent peaks related to chromium are presented in all samples. First, a peak at around $2\theta = 44.3^{\circ}$ corresponds to the (110) peak. Second, the peaks correspond to the (200) and (211) planes at about $2\theta = 64.5^{\circ}$ and 81.7°, respectively. (PDF card, 85-1336).

A difference in the peak's intensity can be noticed. To investigate this deeply, the relative intensity of peaks to the (110) diffraction plane was calculated to analyse changes in texture, presented in Table 8. According to the literature for chromium, the (110), (200) and (211) peaks in Cr powder have relative intensities of 100%, 29% and 16%, respectively.

	XRD absolute intensity (counts)			Rela (1	tive intens 10) plane ('	ity to %)
Plane	110	200	211	110	200	211
Cr (Ref.) ¹⁹²	-	-	-	100	29	16
50V_1h	2363	236	229	100	10	10
75V_1h	3974	413	372	100	10	9
100V_1h	2306	379	333	100	16	14
125V_1h	1669	937	230	100	56	14
150V_1h	766	375	364	100	49	48
200V_1h	793	368	362	100	46	46
250V_1h	368	213	242	100	58	66

Table 8 – Experimental results: XRD absolute intensity and XRD relative intensity to (110) diffraction plane of the Cr-coated samples from -50V to -250V bias voltage.

Overall, the intensity of the (110) plane gradually decreases as the bias voltage increases. However, this increase in bias voltage also results in a significant reduction in film thickness. Therefore, the observed effect on the intensity of the (110) plane for this set of thin films deposited for 1 hour appears to be related to the film thickness, aligning with findings reported in the literature²⁰⁵. Additionally, an increase in the (200) peak and the (211) peak was observed at biases above -125V, indicating a change in the crystallographic texture. These alterations in crystallinity may be attributed to the ion bombardment effect, which becomes more pronounced at higher bias voltages.

Ponte *et al.* reported similar results for chromium coatings using magnetron sputtering with thicknesses between 0.8 and 1.6 μ m. They claimed that the (110) planes have the lowest energy in body-centred cubic structures. In chromium (Cr) films, these (110) planes tend to orient themselves preferentially at the beginning of the film growth process. This happens either because minimizing energy is crucial before the individual islands of the film merge together, or because of competitive growth that occurs as the film continues to form. As the thickness of the films increases, the tops of the columns in the film become larger, and the surface becomes rougher. This increased roughness and larger column tops cause the (110) planes to align more with the tilted surfaces of the film.

6.4 Friction wear test

Figure 65 displays the WLI images after the wear test for the uncoated ZIRLO and the Cr-coated samples from -50V to -100V bias voltage.



Figure 65 – WLI images of the uncoated substrate and Cr-coated samples from -50V to -100V bias with 1h of coating.

Figure 66 displays the WLI images after the wear test for the Cr-coated samples from -125V to -250V bias voltage.



Figure 66 – WLI images of Cr-coated samples from -125V to -250V bias with 1h of coating.

Table 9 present the Cr-coating thickness, wear depth and wear area for the uncoated Zr and the coated samples from NA to -250V for 1h.

Sample ID	Coating time	Cr coating thickness (µm)	Wear depth (µm)	Wear area (µm²)	Wear Rate (mm ³ /Nm)
Uncoated Zr	-	-	7.5	2,792	2.8
50V_1h	1h	1.2	9.4	2,616	2.6
75_1h	1h	1.1	8.1	3,205	3.2
100V_1h	1h	1.0	10.4	5,356	5.4
125V_1h	1h	1.3	7.0	4,724	4.7
150V_1h	1h	0.8	11.3	6,041	6.0
200V_1h	1h	0.5	9.7	4,995	5.0
250V_1h	1h	0.6	12.5	6,668	6.7

 Table 9 – Cr-coating thickness, wear depth and wear area for the uncoated

 ZIRLO and the coated samples from -50V to -250V.

Figure 65 and Figure 66 illustrate the wear tracks produced by the friction wear test, revealing visible damage across all samples. A detailed analysis of the data in Table 9 quantifies the extent of this damage.

Generally, the Cr-coated samples, deposited for 1 hour, demonstrated considerable wear and did not offer substantial substrate protection. Notably, the coating deposited with a -50V bias showed the lowest wear rate, while samples exposed to bias voltages above -100V experienced higher wear rates. This discrepancy in wear rates suggests that the bias voltage, and the coating thickness, significantly influence the protective efficacy of the coatings. It's important to note that the coating thickness is likely to affect substrate protection, indicating that both bias voltage and thickness are crucial contributing factors. However, the exact cause of these effects remains uncertain due to the low coatings' thickness.

Based on these data, it can be inferred that a one-hour coating duration is insufficient to produce a protective thickness for the substrate. Overall, no significant reduction in wear was observed compared to uncoated Zr, and the wear resistance was worse with most of the coatings. The reduced performance observed in the Cr-coated samples may be attributed to the friction caused by hard chromium debris against the material's structure, which likely exacerbates wear.

Therefore, thicker chromium coatings will be produced to understand better the impact of bias voltage on these samples' adhesion and wear resistance.

6.5 Summary

In this chapter, we established the deposition rates of chromium coatings across a range of bias voltages and examined how bias voltage influences structural morphology. An initial friction wear test was conducted to assess the performance of chromium coating deposited for 1h at varying bias voltages.

First, varying bias voltage resulted in differences in the deposition rate. A gradual decrease in the deposition rate was observed with increasing bias voltage, resulting in thinner coatings when the deposition time remained constant. An unexpected result was noted in sample 125V_1h, which displayed the highest deposition rate; however, this anomaly is within the range of standard variation. The decrease in deposition rate is associated with the re-sputtering effect on the surface.

Regarding the coating structure, all samples demonstrated a packed and dense columnar structure. However, the surface morphology undergoes significant changes in shape depending on the bias voltage used. The -50V bias samples exhibit a compact and continuous structure. Dramatic changes are observed in the -75V and - 100V samples, which appear smoother but remain compact and continuous. The surface shape changes from -125V to -250V bias voltages, with a gradual growth of particles and well-defined grain boundaries emerging at -125V. This visual transformation may result from high-energy ion bombardment, increasing atom mobility on the surface and causing small grains to coalesce into larger grains.

The XRD results reveal that the intensity of the (110) plane decreases with increasing bias voltage, which coincides with a significant reduction in film thickness. This suggests that the observed decrease in (110) plane intensity is more closely related to film thickness than to bias voltage, consistent with findings reported in the literature. In addition, the (110) texture weakens at higher bias voltages, suggesting that increased bias may change the coating texture.

About the preliminary friction wear test, all the Cr-coated samples showed significant wear and did not protect the substrate. The coating with a -50V bias exhibited the lowest wear rate, whereas samples with bias voltages exceeding -150V

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had the highest wear rates. This disparity in wear rates might be due to the influence of bias voltage or coating thickness, though the precise cause is undetermined.

These findings suggest that a one-hour coating duration is inadequate for protective thickness. Therefore, the next chapter will be dedicated to investigating thicker chromium coatings to better understand the effect of bias voltage on adhesion and wear resistance.

Chapter 7. Influence of bias voltage and thickness on wear resistance of chromium coatings with 4, 6, and 8-hour deposition times

Chapter 8 analyses the wear resistance of thicker chromium coatings deposited for 4, 6, and 8 hours at -50V, -100V, -150, and -200V bias voltages. The aim of this section is to understand the effects of bias voltage and coating thickness on wear resistance.

7.1 Coatings overview

As found in the previous chapter, thickness is an important parameter to protect the substrate from wear. A 1-hour deposition of Cr coatings may not give adequate protection to the substrate and provide information about the effect of bias on the wear performance.

With the understanding that thickness is a crucial factor in protecting the substrate from wear, we set out to produce thicker coatings in this chapter. Our goal was to assess the influence of bias on wear resistance, a task that thinner coatings were not able to accomplish effectively.

First, the samples were ultrasonically pre-cleaned in acetone for a precise duration of 10 minutes before deposition. Subsequently, the samples underwent sputter cleaning for 15 minutes using a power of 100W and a substrate bias of -650V. Following this preparation, the substrates were coated with chromium for 4, 6, and 8 hours. For this section, the bias voltage values selected to continue the study were: - 50V, -100V, -150V, and -200V.

After the characterization, we assessed the wear resistance of the thicker Crcoatings under the selected bias voltages. We conducted friction wear experiments in a dry environment, using a 6 mm diameter AISI 316 stainless steel ball with a load of 3, 4, and 5N. A frequency of 10Hz was used to create a linear wear track with a full amplitude of 4 mm. We conducted three tests on each sample to calculate the average depth and wear area. The total distance covered was 50 m, which equates to 10 minutes of testing. The conditions of the friction test were chosen according to other studies in the literature^{7,55,56,116}. The samples used included uncoated ZIRLOTM and Cr-coated samples.

7.2 Coating morphology

Table 10 presents information on the sample's identification, deposition time, and thickness according to the bias voltage used.

Sample ID	Deposition time (h)	Bias (V)	Thickness (μm)	Deposition rate (μm/h)
50V_4h	4	-50	5.1 ± 0.1	1.27
100V_4h	4	-100	4.7 ± 0.2	1.18
150V_4h	4	-150	3.0 ± 0.3	0.75
200V_4h	4	-200	2.5 ± 0.2	0.63
50V_6h	6	-50	6.8 ± 0.1	1.13
100V_6h	6	-100	6.3 ± 0.4	1.05
150V_6h	6	-150	4.1 ± 0.1	0.68
200V_6h	6	-200	4.2 ± 0.1	0.70
50V_8h	8	-50	8.7 ± 0.1	1.08
100V_8h	8	-100	7.5 ± 0.1	0.93
150V_8h	8	-150	6.8 ± 0.1	0.85
200V_8h	8	-200	4.1 ± 0.1	0.51

 Table 10 – Sample's information according to bias voltage and deposition

 time.

Figure 67, Figure 68, and Figure 69 present SEM images of the cross-section and top surface of the Cr coatings for bias testing for 4h, 6h, and 8h deposition time, respectively.



Figure 67 – SEM cross-section (10K X) images and thickness of the chromium coatings deposited at -50V to -200V bias voltages for deposition times of 4h, 6h, and 8h.



Figure 68 – SEM cross-section (50K X) images of the chromium coatings deposited at -50V to -200V bias voltages for deposition times of 4h, 6h, and 8h.



Figure 69 – SEM top surface images of the chromium coatings deposited at - 50V to -200V bias voltages for deposition times of 4h, 6h, and 8h.

As expected, the thickness of the coating increased with higher deposition times and decreased with higher bias voltages. The samples $150V_6h$ (Figure 67(h)) and $200V_6h$ (Figure 67 (k)) had practically the same thickness, around 4 μ m. Likewise, the $200V_8h$ sample (Figure 67 (I)) presented a similar thickness to the samples mentioned above.

Surprisingly, the thickness of the 200V_6h sample was greater than expected. The expected deposition rate for a -200V bias is 0.5 μ m/h, as outlined in Chapter 7. However, the observed deposition rate for the 200V_6h sample was 0.7 μ m/h, a difference of 0.2 μ m/h. This discrepancy, which significantly affects the final thickness, may be attributed to slight variations in the sample's position on the substrate holder or minor adjustments in gas flow and total pressure during the deposition experiments.

Regarding the Cr-coating structures, all coatings exhibited a packed and dense columnar structure. However, the films coated at -50V bias voltage look denser and less columnar than those coated at a higher bias. The surface morphology differs significantly, as observed in the 1h deposition samples. The same compact and continuous structure at -50V, then the surface becomes significantly smoother at -100V. Under -150V and 200V bias voltage, the particles gradually grow on the surface with well-defined boundaries between the particles.

7.3 XRD results

Figure 70, Figure 71, and Figure 72 present the X-ray diffraction patterns of the Cr-coated samples from -50V to -200V bias voltage for 4h, 6h, and 8h deposition time, respectively.



Figure 70 – XRD patterns of Cr-coated samples from -50V to -200V bias and deposition time of 4h.

6h coating



Figure 71 – XRD patterns of Cr-coated samples from -50V to -200V bias and deposition time of 6h.



Figure 72 – XRD patterns of Cr-coated samples from -50V to -200V bias and deposition time of 8h.

Table 11 shows the absolute and relative intensities of the (110) diffraction plane. Comparing the relative peak intensities for the (110), (200), and (211) indicates that all the Cr coatings showed the strongest (110) texture compared to reference values for chromium. According to the literature for chromium, the (110), (200) and (211) peaks in Cr powder have relative intensities of 100%, 29% and 16%, respectively.

	XRD absolute intensity (counts)			Rela (1	tive intens 10) plane ('	ity to %)
Plane	110	200	211	110	200	211
Cr (Ref.) ¹⁹²	-	-	-	100	29	16
50V_4h	19764	2514	2745	100	13	14
100V_4h	23404	3817	3163	100	16	14
150V_4h	20702	4648	4145	100	22	20
200V_4h	12180	2214	2908	100	18	24
50V_6h	26505	4305	4356	100	16	16
100V_6h	4340	1495	1085	100	34	25
150V_6h	23667	2667	4102	100	11	17
200V_6h	14197	1891	2345	100	13	17
50V_8h	3390	775	930	100	23	27
100V_8h	3205	980	855	100	31	27
150V_8h	4286	815	925	100	19	22
200V_8h	2235	610	570	100	27	26

Table 11 – Experimental results: XRD absolute intensity and XRD relative intensity to (110) diffraction plane of the Cr-coated samples from -50V to -250V bias voltage

All the samples coated at 4h, 6h, and 8h showed the three prominent peaks characteristics of chromium: the peak at around $2\theta = 44.3^{\circ}$ corresponding to the (110) peak, and the peaks at about $2\theta = 64.5^{\circ}$ and 81.7° correspond to the (200) and (211) planes, respectively (PDF card, 85-1336).

Moreover, the (110) plane was the preferable orientation for all coating. As Gautier *et al.* discuss, the (110) plane is expected to be the preferred orientation due to its highest reticular density of 1.414 atoms/a². In contrast, the other observed planes have lower densities, with the (200) plane at 1 atom/a² and the (211) plane at 0.81 atoms/a². The findings in this work are consistent with these predictions.

Feng *et al.* investigation observed a texture change from (200) at low bias to a (110) texture with increasing bias for chromium coating²⁰⁶. Although the voltage does

not follow a monotonous relationship with crystallinity in this work, we observed that the use of bias voltage favoured the (110) texture.

However, some notable observations can be made. The sample 50V_4h exhibited the most pronounced (110) texture compared to the chromium reference values. This is because the relative intensities of the (200) and (211) textures are the lowest. On the other hand, the 100V_6h showed a noticeable decrease of the (110) peak intensity compared to the 6h deposition group, leading to the lowest (110) texture among the samples.

Moreover, the absolute intensity of the coatings deposited with -200V bias voltage generally exhibited the lowest intensity for all textures. Meng *et al.* discussed the changes observed in the chromium texture using magnetron sputtering and varied bias²⁰⁷. They mentioned that a gradual rise in the bias voltage negatively impacts chromium's crystallinity, reducing both (110) and (200) peaks. Wang *et al.* also reported a peak diminution with continuous bias increase for chromium coatings, mainly from -90V to -150V bias voltage¹¹⁶. Both studies cited above claimed that excessively high bias voltage leads to an overload of energy, which hampers the energy deposition process and obstructs the formation of the (110) texture. Therefore, the deposition conditions used in this work indicated that a -200V bias voltage may be the limit at which the bias voltage begins to be detrimental to (110) formation.

7.4 Hardness and elastic modulus

Table 12 present the experimental values of hardness (H), elastic modulus (E), the maximum indenter depth (hmax), and H/E ratio for the Cr-coated samples from - 50V to -200V bias voltage and deposition times of 4h, 6h, and 8h.

To enhance visualization of trends, the data presented in Table 12 have been plotted in the graphs below displayed in Figure 73.

Sample ID	H (GPa)	E (GPa)	hmax (nm)	H/E
50V - 4h	14.9 ± 1.7	343 ± 45	331 ± 17	0.043
100V - 4h	8.1 ± 0.9	322 ± 41	420 ± 22	0.025
150V - 4h	8.7 ± 1.4	305 ± 33	289 ± 19	0.029
200V - 4h	11.1 ± 2.9	295 ± 45	266 ± 27	0.038
50V - 6h	12.1 ± 1.8	314 ± 46	465 ± 34	0.039
100V - 6h	6.9 ± 1.0	318 ± 41	593 ± 43	0.022
150V - 6h	7.7 ± 1.3	288 ± 37	435 ± 34	0.027
200V - 6h	10.3 ± 2.2	295 ± 45	352 ± 33	0.035
50V - 8h	12.3 ± 2.1	361 ± 66	458 ± 38	0.034
100V - 8h	8.7 ± 1.0	333 ± 23	532 ± 26	0.026
150V - 8h	7.8 ± 1.2	284 ± 33	568 ± 39	0.027
200V - 8h	10.9 ± 2.5	316 ± 61	344 ± 35	0.034

Table 12 – Hardness, elastic modulus, maximum depth, and H/E ratio for the Cr-coated samples from -50V to -200V bias voltage and deposition times of for 4h, 6h, and 8h.



Figure 73 – Hardness, elastic modulus, and H/E ratio charts for the Cr-coated samples from -50V to -200V bias voltage and deposition times of for 4h, 6h, and 8h.

Hardness (H) is the primary mechanical property that determines the wear resistance of materials. Additionally, Young's modulus (E) has been found to affect wear resistance. Furthermore, it is important to consider the H/E ratio once it has been reported in the literature as an indicator of wear resistance. Usually, the higher the H/E ratio, greater the wear resistance^{208,209}.

Generally speaking, the hardness response exhibited a pattern according to the bias voltage for all deposition times. The 50V bias voltage initially presented the highest hardness values at approximately 13 GPa. This was followed by a decrease to around 8 GPa for the 100V and 150V bias voltages. At the highest bias voltage of - 200V, the hardness increased to approximately 10 GPa. Similarly, the H/E ratio follows the same trend. These results suggest that the coatings at -50V bias voltage have the highest wear resistance for presenting the highest ratio, followed by -200V, then -150V and -100V. On the other hand, the modulus of elasticity exhibits a slight decrease with increasing bias, except in the 200V_8h sample.

Table 13 also includes the thickness, (110), (200) and (211) plane relative intensities, hardness, and H/E ratio of all samples, organized by bias voltage. This arrangement facilitates the comparison of these properties based on the bias voltage used rather than the deposition time.

	Thickness	Relative intensity to (110) plane (%)			H (GPa)	H/E ratio
Plane		110	200	211	(GFa)	Tatio
50V_4h	5.1	100	13	14	14.9	0.043
50V_6h	6.8	100	16	16	12.1	0.039
50V_8h	8.7	100	23	27	12.3	0.034
100V_4h	4.7	100	16	14	8.1	0.025
100V_6h	6.3	100	34	25	6.9	0.022
100V_8h	7.5	100	31	27	8.7	0.026
150V_4h	3.0	100	22	20	8.7	0.029
150V_6h	4.1	100	11	17	7.7	0.027
150V_8h	6.8	100	19	22	7.8	0.027
200V_4h	2.5	100	18	24	11.1	0.038
200V_6h	4.2	100	13	17	10.3	0.035
200V_8h	4.1	100	27	26	10.9	0.034

Table 13 – Thickness, hardness, peak relative intensity, H/E ratio, for the Crcoated samples from -50V to -200V bias voltage and deposition time of for 4h, 6h. and 8h.

As can be seen in red, the 50V_4h sample demonstrated the strongest (110) texture, the highest hardness and H/E ratio. Meanwhile, 100V_6h sample demonstrated one of the weakest (110) textures, the lowest hardness and H/E ratio in the group.

As is well known, several factors influence film hardness, including microstructure, grain size, and internal stress. An investigation into some of these factors was conducted to better understand the observed hardness behaviour.

Meng *et al.* discuss a critical fact about the Cr (110) plane, how it is affected by bias voltage and its influence on the structure. Meng *et al.*'s study shows how bias voltage can influence the coating texture and harm crystallinity at higher values. They propose that modulating the chromium texture to achieve the highest reticular density could be beneficial. The (110) orientation, with the highest lattice density of 1.414 atoms/a², is suggested as the most advantageous for chromium coatings featuring body-centred cubic (BCC) lattices. We hypothesise that this orientation, due to its higher plane density, may be one of the factors collaborating to enhance the overall structure density²⁰⁷.

For instance, Chen *et al.* reported the highest hardness at a bias voltage of -150V, corresponding to the presence of the (110) plane with the highest intensity¹⁰⁴. Similarly, an investigation conducted by Wang *et al.* demonstrated higher hardness in a bias voltage of -90V which exhibits greater crystallinity in the (110) texture²¹⁰. Both cited studies used magnetron sputtering as a fabrication method but with different techniques: Chen *et al.* used High-Power Impulse Magnetron Sputtering (HIPIMS), and Wang *et al.* employed Radio Frequency Magnetron Sputtering (RFMS).

In this work, we observed that the sample 50V_4h with the highest (110)/(200) texture ratio with the highest network density was the hardest. Likewise, the opposite was true for the sample 100V_6h. However, this observation appears to be inconsistent among the samples, which shows that it is unlikely that only one factor influences the hardness of the samples.

The hardness of a material is correlated with grain size according to the Hall-Petch relationship, which claims that hardness increases as grain size decreases¹⁸³. Therefore, the influence of grain size on hardness will be discussed in Chapter 8, where TEM images of selected samples will be presented.

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The friction wear tests will be presented in the next sequence, and then the mechanical properties found in this sub-section will be compared and discussed according to the tribological behaviour.

7.5 Friction wear test

Table 13, Table 14, and Table 15 give the wear depth, wear area, and the calculated wear rate for all samples for the 3N, 4N, and 5N loads wear tests, respectively. Additionally, the wear depth and wear rate values were plotted according to the deposition time and load used during the friction test. All charts are gathered in Figure 74 and Figure 75. Throughout each chart, a red point indicated the wear depth of the uncoated substrate.

3N				
Sample ID	Cr coating thickness (µm)	Wear depth (µm)	Wear area (µm²)	Wear Rate (mm ³ /Nm)
Uncoated Zr	-	28.3	17800	71.20
50V_4h	5.1 ± 0.1	13.3	6281	2.10
100V_4h	4.7 ± 0.2	1.3	191	0.10
150V_4h	3.0 ± 0.3	15.0	2052	0.70
200V_4h	2.5 ± 0.2	18.0	5858	2.00
50V_6h	6.8 ± 0.1	0.0	0	0.00
100V_6h	6.3 ± 0.4	2.4	326	0.10
150V_6h	4.1 ± 0.1	0.6	70	0.02
200V_6h	4.2 ± 0.1	0.0	0	0.00
50V_8h	8.7 ± 0.1	0.0	0	0.00
100V_8h	7.5 ± 0.1	1.7	231	0.08
150V_8h	6.8 ± 0.1	1.4	162	0.05
200V_8h	4.1 ± 0.1	0.0	0	0.00

 Table 14 – Results for 3N wear test for the uncoated ZIRLO and the Cr-coated samples from -50V to -250V bias.

4N				
Sample ID	Cr coating thickness (µm)	Wear depth (µm)	Wear area (µm²)	Wear Rate (mm ³ /Nm)
Uncoated Zr	-	30.8	26860	107.00
50V_4h	5.1 ± 0.1	24.7	16087	4.00
100V_4h	4.7 ± 0.2	2.0	282	0.10
150V_4h	3.0 ± 0.3	26.5	14071	3.50
200V_4h	2.5 ± 0.2	24.7	13300	3.30
50V_6h	6.8 ± 0.1	0.0	0.0	0.00
100V_6h	6.3 ± 0.4	2.3	886	0.20
150V_6h	4.1 ± 0.1	16.7	3991	1.00
200V_6h	4.2 ± 0.1	26.3	12005	3.00
50V_8h	8.7 ± 0.1	0.0	0	0.00
100V_8h	7.5 ± 0.1	2.4	95	0.02
150V_8h	6.8 ± 0.1	3.1	228	0.06
200V_8h	4.1 ± 0.1	0.8	0	0.00

 Table 15 – Results for 4N wear test for the uncoated ZIRLO and the Cr-coated samples from -50V to -250V bias.

 Table 16 – Results for 5N wear test for the uncoated ZIRLO and the Cr-coated samples from -50V to -250V bias.

5N				
Sample ID	Cr coating thickness (µm)	Wear depth (µm)	Wear area (µm²)	Wear Rate (mm ³ /Nm)
Uncoated Zr	-	32.9	30330	121.30
50V_4h	5.1 ± 0.1	27.7	22020	4.40
100V_4h	4.7 ± 0.2	30.0	11045	2.20
150V_4h	3.0 ± 0.3	28.3	26535	5.30
200V_4h	2.5 ± 0.2	26.7	16833	3.40
50V_6h	6.8 ± 0.1	0.0	0.0	0.00
100V_6h	6.3 ± 0.4	14.9	4292	0.90
150V_6h	4.1 ± 0.1	16.0	11390	2.30
200V_6h	4.2 ± 0.1	24.7	13199	2.60
50V_8h	8.7 ± 0.1	0.0	0	0.00
100V_8h	7.5 ± 0.1	3.8	805	0.20
150V_8h	6.8 ± 0.1	2.5	558	0.10
200V_8h	4.1 ± 0.1	1.1	112	0.02

The wear depth and wear rate values were plotted according to the deposition time and load used during the friction test. All charts are gathered in Figure 74 and Figure 75. Throughout each chart, a red point indicated the wear depth or wear rate of the uncoated substrate.



Figure 74 – Wear depth graphs for the friction wear tests conducted at 3, 4, and 5 N for the uncoated ZIRLO (indicated by red points) and the Cr-coated samples deposited at bias voltages from -50V to -250V.



Figure 75 – Wear rate graphs for the friction wear tests conducted at 3, 4, and 5 N for the uncoated ZIRLO (indicated by red points) and the Cr-coated samples deposited at bias voltages from -50V to -250V.

Although both the wear depth and wear rate graphs exhibit similar trends, the wear depth provides a clearer visualization of the point at which the coating is fully worn through and the substrate becomes exposed, whereas the wear rate offers more detailed insight into the overall wear behaviour.

Overall, the uncoated substrate consistently exhibited higher wear depths than the coated samples, highlighting the effectiveness of the chromium coatings. The wear rates of the uncoated substrates are also significantly higher than those of the Crcoated samples. When the wear depth and plotted in the charts are compared, it is evident that the tribological behaviour varies according to coating thickness, bias voltage, and applied load.

First, the 4-hour deposition coatings are not protective at any bias voltage. The wear depth of most of these samples significantly exceeded the coating thickness, except for the sample 100V_4h, which showed unexpected behaviour. It demonstrated

reasonable protection at 3N and 4N loads but performed the worst at 5N loads among the 4-hour coatings. These results suggest that the chromium films were not thick enough to provide significant wear protection to the substrate. Therefore, thicker coatings were produced for further analysis.

Next, the 6-hour coatings underwent the same friction test, revealing noticeable differences in wear behaviour. These samples proved protective at the 3N load test but gradually increased wear depth with increasing bias voltage at 4N and 5N loads. From -150V bias onwards, the wear damage penetrated through the coating thickness at 3N and 4N loads, and for 5N loads, the coating depth was breached from -100V bias. No coating wear was observed at -50V bias, providing the best results. However, these findings could also be attributed to the thickness, as there is a decreasing difference in wear depth with increasing bias voltage. Consequently, coatings with 8-hour deposition were prepared further to evaluate the effect of thickness and bias on wear resistance.

Finally, the 8-hour deposition coatings demonstrated the best wear resistance. None of these coatings exhibited wear depths exceeding their thickness. Additionally, it is noticeable that the wear depth is lower for the samples with -50V and -200V bias at all tested loads. Not coincidentally, these two samples also showed the most promising results regarding wear resistance, according to hardness and H/E ratio indices presented previously. Similarly, the -100V and -150V samples demonstrated the lowest wear resistance potential and worse experimental results in these conditions. Therefore, the friction wear tests align with the mechanical properties of the chromium coatings.

Comparing the wear rates, in general, the results suggest that the wear rate of chromium coatings is highly dependent on both the deposition time and the applied bias voltage. Longer deposition times generally lead to lower wear rates, and an optimal bias voltage (likely -50V bias) can further enhance this property.

It is interesting to observe that at the highest load of 5N, the 100V_8h and 150V_8h samples exhibited the highest wear rates among the 8-hour coatings. However, comparisons between these coatings are unfair because of significant differences in thickness: the 100V_8h and 150V_8h samples are more than 1.5 microns thinner than the 50V_8h sample. Consequently, it remains unclear if the observed higher wear rates are an effect of the bias or the thickness.

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Additionally, the 200V_8h coating is half the thickness of the 50V_8h coating, yet it surprisingly provides better wear rate than those deposited at intermediate bias voltages. Even though the 200V_8h starts to show signs of wear at 5N, it is difficult to judge if it is a thickness or bias effect.

Once again, the samples labelled 50V_4h and 100V_6h reveal certain behaviours that merit further attention. Despite its greater hardness, the 50V_4h sample performed worse than the 100V_6h sample under all tested loads. The thickness difference between these samples exceeds 1 μ m, underscoring the importance of an appropriate thickness for chrome protective coatings.

Furthermore, analysis of the wear track images obtained from WLI reveals significant differences between these two samples. Figure 76, for instance, illustrates the 5N test for both samples. It is evident that the entire coating has broken off during the wear test of the 50V_4h sample, as indicated in black arrows in Figure 76. In contrast, the 100V_6h sample shows that the coating gradually wore away throughout the test, resulting in less overall wear. These findings suggest that high hardness also might impart greater brittleness to the material. Additionally, the combination of high hardness and insufficient thickness in the 50V_4h sample is ineffective for a protective coating.



Figure 76 – WLP images of the 5N friction test for 50V_4h and 100V_6h samples. Black arrows in the 50V_4h sample indicate regions where the entire coating has broken off.

Overall, the results presented in this section gave the following answers: First, the chrome coating significantly improved the samples' protection against friction wear compared to the uncoated zirconium substrate. Second, deposition time and, consequently, coating thickness significantly affect coating performance in terms of wear resistance. Thirdly, while the wear rate varies with the bias used, the coatings' thicknesses also differ. This complexity underscores the need for further investigation to determine whether the bias or the coating thickness is the primary influencer of wear resistance.

7.6 Summary

This chapter discussed the wear resistance in chromium coating deposited for 4, 6, and 8 hours at -50V, -100V, -150V, and -200V bias voltage.

Regarding the Cr-coating structures, the longer deposition time generally results in a thicker chromium coating, although thickness reduces with increasing bias. All coatings exhibited a packed and dense columnar structure. In addition, the XRD patterns of all coatings consistently displayed characteristic chromium peaks, with the (110) texture being the strongest one.

The different bias-coated samples also demonstrated different mechanical properties. The highest hardness values were for the coated samples at -50V with about 13 GPa, followed by -200V at around 10 GPa. Then, the Cr-coated samples at -100V and -150V presented similar hardness around 8 GPa. The H/E ratio followed the same pattern as the hardness, indicating that the coatings at -50V bias voltage have the highest wear resistance, followed by -200V, then -150V and -100V. On the other hand, the modulus of elasticity exhibits a slight decrease with increasing bias, except in the 200V 8h sample.

Based on the friction test results presented in this section, some conclusions can be drawn:

- 1. The chromium coatings significantly improved the samples' protection against friction wear compared to the uncoated zirconium substrate.
- Our study found that the Cr coating thickness significantly impacts the tribological performance. Additionally, we observed the best results in Crcoating coating with or above 6μm.
- Although differences in the mechanical assessments can be noticed, the effect of bias voltage on wear resistance could not be assessed properly due to the different coating thicknesses.

Therefore, coatings with similar thicknesses from this chapter were selected and will be compared in the next chapter. Additionally, a more in-depth analysis was conducted on these specific samples to understand the effect of bias voltage. This analysis included scratch tests, Vickers hardness tests, and transmission electron microscopy (TEM) examination.

Chapter 8. Influence of bias voltage on wear resistance of chromium coatings with similar thickness

Chapter 9 examines the wear resistance of chromium coatings with a similar thickness of approximately 6 μ m, deposited at bias voltages of -50V, -100V, and - 150V. Additionally, a coating with no applied bias (NBA) was produced for comparison with the biased coatings. The aim of this section is to determine the optimal bias voltage for maximizing wear resistance.

8.1 Coating overview

In the previous chapter, it was not possible to determine the optimal bias voltage for wear resistance due to variations in coating thickness. Therefore, in this chapter, chromium coatings with similar thicknesses of more than 6 μ m were selected for assessment. Furthermore, additional characterizations and tests were performed on these selected coatings to better understand the effect of bias voltage.

The samples were ultrasonically pre-cleaned in acetone for 10 minutes before deposition. Subsequently, all the samples underwent sputter cleaning for 15 minutes at -650V, with a working pressure of 0.36 Pa. Samples were coated with no bias applied (NBA), i.e., at floating potential, followed by applied DC biases of -50V, -100V, and -150V.

For these samples, additional characterizations included focused ion beam SEM (FIB-SEM) images, scanning transmission electron microscopy (STEM) images of the coating cross-sections, AFM, and SEM images of the wear tracks. Additionally, the coatings' toughness was qualitatively assessed by inducing cracks using a Vickers hardness tester equipped with a diamond indenter, applying loads of 30 kgf. The adhesion strength of the Cr coatings was evaluated using scratch testing. During scratch testing, the normal load applied to the coating gradually increased from 0 N to 30 N at a rate of 40 N/min, over a scratch length of 3 mm. The normal load, acoustic signal, and penetration depth were recorded by the tester during scratch testing.

8.2 Coating morphology

Table 17 presents information on the sample's identification, bias voltage, coating time, thickness, deposition rate for each sample. Figure 77 presents the top surface SEM images of selected coatings.

Table 17 – Samples ID, coating time, thickness, and deposition rate of the NBA, -50, 100 and 150V coating.

Sample ID	Bias voltage (V)	Coating time (h)	Thickness (μm)	Deposition rate (μm/h)
Cr_NBA_6.9µm	No bias applied	6h	6.9 ± 0.2	1.15
Cr_50V_6.8µm	-50V	6h	6.8 ± 0.1	1.13
Cr_100V_6.3µm	-100V	6h	6.3 ± 0.4	1.05
Cr_150V_6.8µm	-150V	8h	6.8 ± 0.1	0.85



Figure 77 – SEM top surface images of chromium coatings deposited with (a) NBA, (b) -50V, (c) -100V and (d) -150V bias.

As can be seen in the images, the surface morphology differs significantly in shape and grain size based on the bias voltage used. The no bias applied (NBA) coating (1a) exhibited a pyramid structure of varying sizes that originated from the columnar structure. In addition, gaps or pores can be observed between the columns. Increasing to -50V bias voltage (73b) significantly changes the coating structure; the surface morphology became smoother. It is also observed that the surface looks dense and uniform, without any gaps. When the voltage is increased to -100V, (73c) the surface is even smoother, still dense and remains similar at -150V bias (73d). Although the surface is continuous and uniform, defined boundaries and grains are formed on the surface. These results might be a consequence of the high-energy of the incident ion bombardment that leads to a higher mobility of the atoms at the surface. Then, small grains merge, resulting in a larger grain size^{189,190}.

The same surface morphology trend can be observed in the AFM images, as illustrated in Figure 78.



Figure 78 – AFM images of chromium coatings deposited with (a) NBA, (b) - 50V, (c) -100V and (d)-150V bias coatings.

In addition, the AFM also provides surface roughness values (Ra), as can be seen in Table 18. The NBA sample showed a roughness of 31.0 ± 5.7 nm, which was the highest values comparing with the other coatings, probably this is related to the

irregular surface created by the columnar grains. The coatings deposited at -50V, -100V and -150V bias voltage all present similar roughness values in the range 15 to 19 nm, which confirms their broadly similar surface appearance.

Sample ID	AFM roughness Ra (nm)
Cr_NBA_6.9µm	31.1 ± 5.7
Cr_50V_6.8µm	19.6 ± 7.1
Cr_100V_6.3µm	15.3 ± 3.2
Cr_150V_6.8µm	17.3 ± 2.1

Table 18 – Roughness of the NBA, -50, 100 and 150V coating.

Figure 79 presents the SEM images of the FIB cut outs of the chromium coatings deposited with NBA, -50V, -100V, and -150V bias.



Figure 79 – STEM images of the FIB cut out of chromium coatings deposited under bias voltages of (a) NBA, (b) -50V, (c) -100V, and (d) -150V.
In agreement with the top surface images (see Figure 77), the NBA sample (a) presented a porous columnar structure. Meanwhile, the films coated with -50V (b), - 100V (c) and -150V (d) bias voltages demonstrated much denser structures.

Comparing the no bias applied coating with the others, the bias voltage densification effect is evident. When bias voltage is applied on the substrate, the atoms reach the surface with higher kinetic energy and have more energy to diffuse, forming more organized, denser structures.

Figure 80 shows the electron backscatter diffraction (EBSD) analyses of Cr coatings deposited under bias voltages of (a) -50V, (b) -100V, and (c) -150V. Figure 81 and Figure 82 present the TEM images of the Cr coatings deposited under bias voltages of (a) NBA, (b)-50V, (c) -100V, and (d) -150V.



Figure 80 – Cross-section EBSD analyses of the chromium coatings deposited under bias voltages of (a) -50V, (b) -100V, and (c) -150V. The colours triangle indicates the crystallographic directions, typically red for (001), green for)101), and blue for (111).



Figure 81 – Low magnification TEM images of the cross-sections of Cr coatings deposited under bias voltages of (a) NBA, (b)-50V, (c) -100V, and (d) - 150V.



Figure 82 – High magnification TEM images of the cross-sections of Cr coatings deposited under bias voltages of (a) NBA, (b)-50V, (c) -100V, and (d) -150V.

Table 19 displays the grains widths measurements of the grains near the top surface using the image software ImageJ, about 20 grains were measured. Additionally, the grain aspect ratio was calculated and are displayed in Table 19. The grain aspect ratio can indicate the shape of the grains: an aspect ratio closer to 1 indicates a more circular shape, while lower values suggest a more columnar grain structure.

Sample ID	Grain size (nm)	Grain aspect ratio
Cr_50V_6.8µm	80 ± 42	0.4 ± 0.2
Cr_100V_6.3µm	171 ± 89	0.5 ± 0.3
Cr_150V_6.8µm	190 ± 59	0.2 ± 0.1

Table 19 – Grain size and grain aspect ratio of the cross-sections of Cr coatings deposited under bias voltages of (a)-50V, (b) -100V, and (c) -150V.

The STEM images in Figure 75 reveals variation in the microstructure and morphology according to the bias voltage used. The NBA sample exhibited a long, porous columnar structure, which also displayed a triangular shape at the surface edges due to the pyramidal structure. The samples coated under -50, -100V, and - 150V bias voltage show a columnar and dense structure.

A significant change in grain size and shape was observed in response to the different bias voltages applied, as evidenced by the EBSD and TEM analyses. EBSD analysis was not performed on the NBA samples because they exhibited a columnar structure with gaps, and no grain boundaries were observed within these columns. The grains exhibit a columnar and elongated shape for the coatings deposited with bias voltage, particularly in the -150V Cr coating. This shape is confirmed by the grain aspect ratio values, which is the ratio between the width and length of the grain. Therefore, the sample deposited at -150V with the lower aspect ratio has more columnar grains than those deposited at -50V and -100V.

Regarding the bias voltage effect on the grain size, the analyses revealed much smaller grains in the Cr_50V_6.8µm samples. As the bias voltage increased, the grains became larger and more elongated. Measurements of grain width near the surface showed a gradual increase with the rising bias voltage. The grain width of the Cr coating deposited at -50V was less than half that of the coating deposited at -100V, measuring 80 nm and 171 nm, respectively. Meanwhile, the coating deposited at - 150V had grains only about 20 nm larger than those in the -100V sample.

Similar findings were reported in the study by Zhu *et al.*, which examined the effects of bias voltage on the microstructure and steam oxidation behaviour of sputtered Cr coatings. They tested Cr coatings under no bias and at bias voltages of -50V, -100V, and -150V, observing a gradual increase in grain size with increasing bias voltage. They attributed the influence of bias voltage on grain size to two primary

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factors. First, a negative bias introduces more defects into the matrix due to ion bombardment, leading to an increased number of nucleation sites and smaller grains. Second, higher bias voltage can raise the substrate temperature, enhancing the diffusion capability of atoms and grain boundaries, which promotes grain fusion and increases grain size. Consequently, the substrate temperature is a factor that is likely contributing to grain size growth²².

To better understand the effect of bias voltage on substrate temperature, measurements were taken using a thermocouple at the two extreme bias values used in this chapter: -50V and -150V. The temperatures were recorded after 1 hour of deposition, and the results are presented in Figure 83.



Figure 83 – Substrate temperature during the deposition of the Cr coatings at - 50V and -150V bias voltage.

As reported in the literature, increasing the bias voltage causes the substrate temperature to rise. In this study, raising the bias from -50V to -150V led to a temperature increase of about 30 °C. This added thermal energy improved atomic mobility and diffusion at the grain boundaries, which contributed to the grain growth observed in the STEM results²².

8.3 XRD



Figure 84 presents the X-ray spectra results for the NBA, -50V, -100V, and - 150V samples.

Figure 84 – X-ray spectra of Cr films coated at NBA, -50V, -100V and -150V.

All the films presented a peak at around $2\theta = 44.3^{\circ}$, corresponding to the (110) peak, although for the NBA sample, the (110) peak is very low intensity and almost imperceptible when shown on the same scale as the applied biased samples, hence the insert showing the peak region magnified. In addition, coatings deposited at -50V, -100V, and -150V bias presented lower intensity peaks corresponding to the (200) and (211) planes at about $2\theta = 64.5^{\circ}$ and 81.7° (PDF card, 85-1336).

Analysing the relative peak heights for the (110), (200), and (211) planes in Table 20 reveals that the -50V coating exhibits the most pronounced (110) texture compared to the reference values for chromium.

intensity to (110) diffraction plane).						
	XRD absolute intensity (counts)		Relativ	e intensity plane (%)	to (110)	
Plane	(110)	(200)	(211)	(110)	(200)	(211)
Cr (Ref.) ¹⁹²	-	-	-	100	29	16
-50V	26505	4305	4356	100	16	16
-100V	4340	1495	1085	100	34	25
-150V	4286	815	925	100	19	22

 Table 20 – Experimental results (XRD absolute intensity and XRD relative intensity to (110) diffraction plane).

The Cr-coatings with similar thickness showed different peak intensities according to the bias applied. In general, the preferred peak was the (110) plane. Some studies observed a shift in texture from the (110) to (200) plane as the bias rose^{152,207,210}, which was observed here, but only to a small degree.

The texture evolution is highly dependent on the temperature, argon pressure and bias voltage. Feng *et al.* investigated deeply the effect of the crystallographic texture of Cr films varying some deposition parameters, including pressure, bias and substrate temperature. They reported that higher temperatures benefited the (200) texture, while the bias promotes the (110) texture. Hence, the transition to the (200) plane under high bias may also occur due to inherent surface heating resulting from increased bias levels. However, in this study, it appears that the bias effects were more relevant than the process heating caused by the bias, which was not significant regarding texture shift²⁰⁶.

The Table 21 presents the nano-hardness, elastic modulus, and H/E ratio of the NBA, -50, 100 and 150V bias voltage Cr-coated samples.

Sample ID	Hardness (GPa)	Elastic modulus (GPa)	H/E ratio
Zr uncoated	4.0 ± 0.8	118 ± 14	-
NBA_6.9µm	3.5 ± 0.6	149 ± 25	0.023
50V_6.8µm	12.1 ± 1.8	314 ± 46	0.039
100V_6.3µm	6.9 ± 1.0	318 ± 41	0.022
150V_6.8µm	7.8 ± 1.2	284 ± 33	0.027

Table 21 – Hardness, elastic modulus, and H/E ratio of the NBA, -50, 100 and150V bias voltage coating.

The Figure 85 presents the nano-hardness, elastic modulus, and H/E ratio graphs of the NBA, -50, 100 and 150V bias voltage Cr-coated samples



Figure 85 – Graphs of hardness, elastic modulus, and H/E ratio of the NBA, -50, 100 and 150V bias voltage coating.

The nano-hardness results revealed relevant findings about the influence of the different bias voltages, as detailed in Table 21 and Figure 85. The NBA coating exhibited the lowest hardness among the Cr films, measuring 3.5 GPa. However, this

sample featured a columnar grain structure with gaps, which may have caused the indentation deformation to pass through these empty spaces, leading to lower hardness measurements. As a result, the reported hardness may not accurately reflect the true hardness of the bulk material due to the porous structure.

In contrast, the -50V bias coating presented the highest hardness among the samples at 12GPa. A significant change was noticed from -50V to -100V and -150V bias voltage, in which the hardness decreased from 12.1 GPa to 7-8 GPa.

The hardness of a material is correlated with grain size according to the Hall-Petch relationship, which claims that hardness increases as grain size decreases. Hardness increases because there are more grain boundaries in a structure with smaller grains. These boundaries behave as barriers to grain dislocation. Therefore, the movement of grains is restricted, and the plastic deformation is limited. As a result, the material's strength and hardness are enhanced¹⁸³.

As observed in the TEM images, the Cr coating deposited at -50V exhibited the smallest grain size. In contrast, the grain size more than doubled for the samples deposited at -100V and -150V. The latter two samples demonstrated minimal differences in both hardness and grain size.

When it comes to the elasticity modulus, the Cr-coatings exhibited a different fluctuation compared to the hardness. NBA coating exhibited an elastic modulus of 149 GPa. Meanwhile, the coatings using -50V and -100V showed similar values an increasing to 314 GPa and 318GPa, respectively. Next, -150V bias voltage coating presented a fall to 284 GPa.

Regarding the H/E ratio, the -50V bias voltage coating presented the highest value by 0.04, the other coatings fluctuated around a similar ratio of 0.02. A higher values of H/E ratio could indicate potentially higher wear resistance.

8.4 Mechanical properties assessments

Figure 86 displays a bar graph (a) with the wear rate calculated for each sample and load used, and a line chart (b) illustrating wear depth vs. the load.



Figure 86 – (a) Wear rate, (b) wear depth of the uncoated ZIRLO[™] and Crcoated samples under NBA, -50V, -100V and -150V bias voltage.

Figure 87 exhibits the 3D morphology images of the wear track for each film and load used.



Figure 87 – Surface 3D morphology of the uncoated ZIRLO[™] and Cr-coated samples under NBA, -50V, -100V and -150V bias voltage.

As can be seen in both charts, a notable enhancement is observed when employing Cr films compared to the uncoated sample. The ZIRLOTM showed a high wear rate (about 6 mm³/Nm) and a wear penetration depth of around 30 μ m for all loads tested. As observed in the graphs and image, none of the films wore as much as the zirconium.

Among the Cr-coatings, the NBA condition showed the poorest protection and was rapidly worn through at the higher test loads. This condition presented the highest wear rate for the coated samples, and the wear depth was the greater in comparison with the other Cr films. However, it still protects to some extent when compared with the bare substrate. Therefore, even a porous and columnar Cr-coating performed better than no film.

On the other hand, the best performance was the -50V bias film, as no signs of wear were detected on the surface, leading to zero measurable wear rate over the range tested. Next, the deposition at -100V bias voltage presents slight wear at 3 and 4N, but this film still protects the substrate. However, at 5N the -100V coating is seriously damaged. The wear track penetrated nearly 15 μ m into the sample, which is much greater than the coating thickness (6.3 μ m). Finally, when the bias increased to -150V, although gradual wear climbed with increasing load, the film protected the substrate even at 5N. This coating also exhibits a very low wear rate.

Generally, higher hardness is associated with improved wear resistance, this relationship is observed in this study. The Zr substrate, with a very low hardness of 4 GPa, exhibited poor wear resistance. In contrast, the Cr coating deposited at -50V bias voltage demonstrated the highest hardness, 12.1 GPa, and consequently the best wear performance among this set of samples. Meanwhile, the Cr coatings deposited at -100V and -150V bias voltages showed moderate hardness values between 7 and 8 GPa, but wear began to appear, particularly in the -100V sample.

As mentioned in the literature, the higher values of H/E ratio could mean a potential for higher wear resistance. In this work we observed this trend in the results, once the -50V bias voltage coating presented the highest value by 0.04, and the other coatings fluctuated around a similar ratio of 0.02.

Figure 88 illustrates the EDX mapping carried out on the wear tracks at 3, 4 and 5N loads.



Figure 88 – EDX mapping on the (a) wear track surface of Cr-coated samples and (b) ball scar of the uncoated ZIRLOTM and Cr-coated samples under NBA, - 50V, -100V and -150V bias voltage.

The EDX maps on the wear track show that all the coatings broadly survived the 3N load test and none was completely removed. The maps further show that the NBA coating was removed in the wear track region during the 4N and 5N test and the -100V coating was removed during the 5N test only, as indicated by zirconium (in green) from the substrate being identified by the EDX.

Figure 89 presents the EDX mapping of the ball scar for the 5N load test, which was the most aggressive load.



Figure 89 – EDX mapping on the ball scar of the uncoated ZIRLO[™] and Crcoated samples under NBA, -50V, -100V and -150V bias voltage.

The analysis indicates the presence of zirconium (in green) on the ball where the coating was removed for the no applied bias sample and the coating deposited at a bias voltage of -100V.

Figure 90 shows the SEM micrographs of the wear track regions for the 5N load tests at (a) NBA, (b) -50V, (c) -100V, and (d) -150V, respectively.



Figure 90 – SEM images of the wear track of the 5N load test for Cr-coated samples under (a) NBA, (b) -50V, (c) -100V, and (d) -150V bias voltage.

All the worn surfaces present a contrast in the trail along the wear direction. This dark contrast is the Fe accumulation on the surface, as detected on the EDX analyses shown in pink (Figure 88).

The samples NBA (a) and -100V (c) exhibit wear reaching the substrate, which is evidenced by a change in contrast observed in the centre of the wear tracks. The lighter regions in the wear tracks indicate the presence of zirconium from the substrate, as confirmed by EDX analyses shown in green in Figure 88.

All the worn surfaces presented some debris accumulation among the wear tracks (shown by black arrows). The debris are even more evident on the samples NBA and -100V, in which the wear was severe. In addition, the NBA sample also presented some cracks as shown by black arrows (Figure 90(a)).

Furthermore, in the samples NBA, -100V and -150V, there are some fine and long parallel grooves at the coating's sliding surfaces along the friction direction (shown by black arrows), which seems to be abrasive wear.

EDX mapping analysis were performed in the wear track regions of the 5N test samples to identify the debris. The Cr-coatings at -50V and -100V bias voltage are shown in Figure 91. These two specific samples were selected to illustrate the contrast between the extremes, showing a fully worn surface versus a non-worn surface.



Figure 91 – EDX mapping analyses of the wear track at 5N load test for Crcoated samples under (a) -50V, and (b) -100V bias voltage.

As can be seen, zirconium is presented in green, iron in pink, chromium in blue and oxygen in red. The debris observed in darker spots inside the wear tracks appears to be iron from the ball, as can be seen in pink in the EDX analyses (Figure 91). Figure 91 (a) show the sample deposited under -50V bias voltage and an iron accumulation in the surface can be observed, suggesting that the ball bearing was worn instead of the chromium coating.

On the other hand, Figure 91 (b) shows the sample with a -100V bias voltage, revealing primarily the substrate, which indicates significant wear of the coating. Additionally, debris along the wear track was identified as chromium. It is also evident that oxygen is concentrated in the same areas as chromium, suggesting the formation of a chromium oxide layer. Furthermore, based on the position of the iron identification, it appears that iron debris is accumulating on top of the chromium/chromium oxide layers.

To assess the ability of the Cr coatings in resisting contact damage, Vickers indentations were performed in the coating surfaces at a 30kgf load. Then, SEM images of the indentation morphologies were obtained and are presented in Figure 92.



Figure 92 – Vickers test on the Cr-coated samples (a) NBA, (b) -50V, (c) -100V, and (d) -150V bias voltage. The black arrows indicate the cracks caused by the indenter.

The NBA coating suffered severe delamination, in which the entire surrounding Cr film cracked and delaminated. These results show the poor quality of this columnar coating and low damage resistance.

The -50V film presented long edge cracks (shown by black arrows) and cracks in the middle area of the indenter, indicating a poor damage resistance, which may be attributed to the hard, brittle and poor adhesion strength of the -50V coating.

On the other hand, the -100V coating presented a significantly smoother indented surface in the middle area. Although this sample also exhibits small surface radial cracks in two edges (shown by black arrows), it exhibits good toughness likely because of the lower hardness. Lastly, even though the -150V bias voltage coating

seems smooth in the middle area, it also presents crack patterns in the edges and in the centre lines of the indentation, as indicated by the black arrows. Therefore, the -150V bias voltage coating also showed an insufficient resistance to damage.

Figure 93, Figure 94, Figure 95, and Figure 96 presents the SEM images of the scratch tracks, and the representative curves of acoustic emission signal and penetration depth as a function of the applied normal load obtained in the scratch test for NBA, -50V, -100V, and -150V bias voltage samples, respectively. Figure 93 and Figure 94 also show a EDX map of the specific areas of the scratch test.

The scratch test curves also present the first and the second critical loads denoted as Lc1 and Lc2, respectively. Lc1 and Lc2 are the critical loads estimated from the scratch test, they can be used to determine the cohesive strength and interfacial adhesive strength of the coating, respectively. Lc1 defines the lower critical load corresponding to cracking. It is possible to determine the location of Lc1 by a sudden increase in the acoustic emission spectrum for a normal. On the other hand, Lc2 defines the upper critical load characterised by continuous substrate exposure²¹¹.



Figure 93 – SEM image of the scratch track, and the representative curves of acoustic emission signal and penetration depth obtained in the scratch test for NBA sample.



Figure 94 – SEM image of the scratch track, and the representative curves of acoustic emission signal and penetration depth obtained in the scratch test for -50V bias voltage sample.



Figure 95 – SEM image of the scratch track, and the representative curves of acoustic emission signal and penetration depth obtained in the scratch test for -100V bias voltage sample.



Figure 96 – SEM image of the scratch track, and the representative curves of acoustic emission signal and penetration depth obtained in the scratch test for -150V bias voltage sample.

The critical loads Lc1 and Lc2 values are shown in Table 22.

Sample	Lc ₁ (N)	Lc ₂ (N)
NBA_6.9µm	0.5	28
50V_6.8µm	0.3	9.7
100V_6.3µm	7	-
150V_6.8µm	0.6	-

 Table 22 – Critical load of the scratch test of the Cr-coated samples NBA, -50V,

 -100V, and -150V bias voltage.

The NBA sample presented a sudden peak in the acoustic emission (AE) at the beginning of the scratch test for a normal load of around 0.4N, indicating the initiation of cracks. As the indenter moved from the Lc1 location under progressive loading conditions, the AE showed a fluctuating pattern with several peaks and troughs. These fluctuations could be attributed to cracking events or other forms of stress relief. The AE increases significantly towards the end of the test, which matches the substrate exposition, indicating the Lc2 location at 28N. Cracks along all the scratch lengths were observed in the SEM images. Additionally, the EDX mapping confirmed the presence of Zr from the substrate. The penetration depth (PD) profile of the analysis reveals that the measurements extend significantly into the substrate, reaching nearly 50 microns. Despite this considerable penetration, the coating remains present within the groove created in the substrate. However, there is a slight increase just before the critical failure point.

The Cr coating deposited at -50V bias voltage presented a high initial AE, marking the Lc1 at about 0.3N. Then, the AE present a significant event around 8N, where the emission briefly increases before stabilizing at a lower value. This event is also observed in the PD curve with a noticeable drop. In the SEM images, the initial phase shows minor damage, but as the load increases, significant material removal and cracking occur, particularly in the central region, indicating the Lc2 point (8N). The test ends with severe material failure, marked by substantial cracking and delamination. The EDX mapping showed severe damage in the Cr-coating with an expressive substrate exposure in the central area. Unexpectedly, the substrate exposure was not continuous during the test. The scratch test was repeated three

times, and all presented similar results. The non-continuous substrate exposure can be related to defects in the coating.

The sample coated at -100V bias voltage presented a completely different behaviour. The acoustic emission remains very low, fluctuating around 1-5%. This indicates minimal acoustic activity, suggesting stable contact and less significant microstructural changes or damage compared to previous tests. Although there is a tiny peak around 7N in the AE curve, no cracks or delamination were observed on the SEM images. Regarding the PD, the curve steadily increases, showing smooth and consistent penetration into the material without significant disturbances in the coating groove. The SEM images confirm the -100V coating's behaviour, showing a relatively smooth scratch with minor material displacement.

The -150V bias voltage Cr-coated sample shows multiple peaks and a slight fluctuation in the AE between 1 and 10%. This sample's first and most intense peak is by 0.6N, indicating the Lc1; according to this observation, the SEM images presented small cracks in the initial part of the scratch track. Along the track, more cracks appear spaced out, as do the acoustic emission signals. The penetration depth increases steadily without significant disturbances, as confirmed by the smooth and consistent scratch observed in the SEM images. Although minor material displacement and a few cracks were observed along the track, this sample does not present severe delamination and substrate exposure.

Overall, the adhesion performance of chromium coatings under different bias voltages showed significant variation among the samples. The -100V bias voltage coating emerged as the most effective in terms of adhesion, exhibiting minimal damage and consistent performance. The -150V bias voltage showed minor spaced-out cracks but no severe delamination or significant substrate exposure, suggesting moderate adhesion performance. On the other hand, the NBA and -50V samples showed significant deficiencies. The results highlight the importance of optimizing bias voltage during coating deposition to enhance adhesion and performance.

8.5 Summary

In this chapter, the aim was to investigate and compare the effects of substrate bias voltage on chromium coatings of similar thickness. To achieve this, chromium coatings with an approximate thickness of 6 µm were deposited onto zirconium alloy substrates using pulsed DC magnetron sputtering. The deposition process was conducted under varying substrate DC bias voltages (-50V, -100V, and -150V), as well as under conditions with no applied bias voltage (NBA).

In conclusion, the findings indicate that the Cr-coated ZIRLO[™] significantly improved wear performance compared to the uncoated substrate. Additionally, all bias voltage coatings provided some level of protection, but the Cr-coated ZIRLO[™] at -50V bias voltage exhibited the best wear resistance due to the higher hardness and smaller grains. However, despite its superior wear resistance, the -50V coating had the lower cracking resistance and the worse adhesion to the substrate. On the other hand, the -100V coating offered the highest resistance to deformation and adhesion, but the worse wear resistance among the biased samples.

Chapter 9. Chromium nitride coatings

Chapter 10 proposes a chromium nitride (CrN) as an option to improve the wear resistance of a protective coating to nuclear claddings. This new approach aims to improve the wear resistance since CrN is known as a harder material. Additionally, as Cr coating showed previously a worse wettability then the substrate (Chapter 6), CrN will also be tested in relation to surface wettability.

9.1 Coating overview

Chromium nitride (CrN) has been identified as a competitive candidate for coating zirconium (Zr) alloys. Ceramic materials like CrN are known for their brittleness, high hardness, and excellent thermal and oxidation properties ^{19,20}. In the literature, CrN has been highlighted as more promising than Cr₂N, offering advantages such as higher density and lower wear rates ¹²¹. Consequently, this results section will begin with a composition study to achieve the desired CrN stoichiometry.

Despite their high hardness, CrN coatings have poor adhesion to metal substrates compared with pure Cr coatings. Thus, the adhesion between coating and substrate is achieved by designing a multilayer coating of (Cr/CrN)_n layers. Furthermore, it has been reported that wear resistance was improved when CrN or Cr was combined in a layered structure^{56,120}.

For these reasons, three different Cr/CrN layer configurations were designed for this project. First, a Cr layer was deposited for 3 hours, followed by a CrN deposition for 1 hour. This approach was chosen because, as observed in Chapter 8, a 4-hour Cr coating exhibited poor wear resistance. The goal was to determine if a CrN layer could improve the performance of thinner Cr layers.

Second, given in Chapter 8 that the 6-hour chromium depositions began to show improvements in wear tests, a 4-hour Cr coating was combined with an external CrN layer deposited for 2 hours. This configuration assessed whether a harder coating finish could offer any additional benefits.

Third, an entire CrN film was deposited for 8 hours to compare its performance with the chromium coatings.

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Additionally, previous chapters highlighted significant differences in results between -50V and -100V bias voltages. Therefore, both voltages were tested in each Cr/CrN combination to evaluate their effects.

Table 23 presents information on the sample's identification, bias voltage, coating time, thickness, deposition rate for CrN of each sample. For the samples with the CrN overlayer, the thickness of the CrN coating only is highlighted in red in Table 23.

Sample ID	Bias voltage (V)	Cr Coating time (h)	CrN Coating time (h)	CrN deposition rate (µm/h)	Thickness (μm)
CrN_8h_50V	-50V	-	8h	0.71	5.75 ± 0.06
CrN_8h_100V	-100V	-	8h	0.30	2.39 ± 0.03
Cr4h-CrN2h_50V	-50V	4h	2h	-	6.18 ± 0.06
Cr 4h-CrN 2h_50V CrN layer	-50V	4h	2h	0.69	1.38 ± 0.02
Cr4h- CrN 2h_100V	-100V	4h	2h	-	5.32 ± 0.02
Cr 4h-CrN 2h_100V CrN layer	-100V	4h	2h	0.45	0.9 ± 0.01
Cr3h-CrN 1h_50V	-50V	3h	1h	-	4.35 ± 0.02
Cr3h- CrN1h_50V CrN layer	-50V	3h	1h	0.72	0.72 ± 0.01
Cr 3h-CrN 1h_100V	-100V	3h	1h	-	3.91 ± 0.02
Cr3h-CrN1h_100V CrN layer	-100V	3h	1h	0.64	0.64 ± 0.02

Table 23 – Samples ID, bias voltage, Cr and CrN coating time, total and CrN thickness.

9.2 Composition study for CrN

To investigate the stoichiometry of chromium nitride (CrN), we tested four different nitrogen partial pressures while maintaining a constant argon partial pressure of 1.4 mTorr (0.19 Pa). For this study, the deposition time was fixed at 1 hour. The nitrogen partial pressures and the corresponding atomic percentages obtained from the EDX analyses are presented in Table 23.

Sample ID	Total pressure (mTorr)	N ₂ Partial Pressure (mTorr)	Ar (sccm)	N₂ (sccm)	Chromium At (%)	Nitrogen At (%)
1.6_CrN	1.6	0.2	29	7	68	32
1.7_CrN	1.7	0.3	29	13	53	47
1.8_CrN	1.8	0.4	29	18	50	50
1.9_CrN	1.9	0.5	29	20	49	51

Table 24 – Parameters of partial pressure control study of CrN.

Figure 97 presents the X-ray diffraction (XRD) chart of the CrN composition study samples.



Figure 97 – X-ray spectra of CrN composition study samples.

The sample designated as 1.6_CrN exhibited a composition closer to Cr_2N , nearly double Cr compared to N in atomic proportion, peaks are marked by a red triangle. Regarding the XRD analysis, this sample showed a single peak at approximately $2\theta = 43.1^{\circ}$, which can be attributed to the hexagonal close-packed Cr_2N (200) plane^{212,213}. As the nitrogen flow increased, the composition shifted towards CrN, and the characteristic face-centred cubic (fcc) CrN peaks emerged, peaks are shown in blue squares. The sample 1.7_CrN showed a higher nitrogen concentration, though still lower than Cr, with 50 at% and 47 at%, respectively. The XRD pattern of the 1.7_CrN sample presented two distinct CrN peaks at $2\theta = 43.7^{\circ}$ and 63.5° , corresponding to the (200) and (220) planes, respectively.

The sample 1.8_CrN displayed the exact stoichiometry expected for CrN (50 at% Cr and 50 at% N), along with three prominent XRD peaks of fcc CrN at 37.2°, 43.7°, and 63.5°, corresponding to the (111), (200), and (220) planes. In the last composition test, the sample 1.9_CrN exhibited a composition indicative of CrN stoichiometry. However, it suggested a slightly higher nitrogen content, which may indicate the limit of nitrogen addition during the deposition. This sample showed four peaks corresponding to the fcc CrN structure at 37.2°, 43.7°, 63.5°, and 75.5°, associated with the (111), (200), (220), and (311) planes.

Furthermore, all samples except 1.6_CrN exhibited a peak around $2\theta = 34.7^{\circ}$, marked with a green ball. This peak is not characteristic of CrN or Cr₂N. We hypothesize that this peak is related to the (100) plane of zirconium of the substrate once the sample is relatively thin, at about a few hundred nanometers.

Based on the experimental results, a total pressure of 1.8 mTorr and a nitrogen (N₂) partial pressure of 0.4 mTorr were chosen for the subsequent CrN depositions. The sample deposited under these conditions, labelled 1.8_CrN, exhibited optimal stoichiometry and a well-defined crystalline structure.

9.3 Coating morphology

The Figure 98 presents the SEM top surface images of all Cr/CrN coating configurations.



Figure 98 – SEM top surface images of the CrN films deposited for 8h at -50(a) and -100 bias (b), Cr+CrN films deposited for 6h at -50(c) and -100 bias (d), and Cr+CrN films deposited for 4h at -50(e) and -100 bias (f).

As observed in Chapters 8 and 9, different biases significantly change the coating grain shape. First, the -50V bias voltage depositions presented grain structures that were more distinct and elongated. The grains also exhibit triangular edges protruding from the surface. Even so, the surface appears to be densely packed. On the other hand, the -100V bias voltage samples looks compact and continuous but smoother than the -50V bias samples.

Figure 99 presents the SEM cross-section images of all Cr/CrN coating configurations. A red line indicates the interface between the Cr and CrN coatings on the samples with a CrN top layer over the Cr.



Figure 99 – SEM cross-section images of the CrN films deposited for 8h at -50(a) and -100 bias (b), Cr+CrN films deposited for 6h at -50(c) and -100 bias (d), and Cr+CrN films deposited for 4h at -50(e) and -100 bias (f).

The CrN coating applied for 8 hours showed a thickness of 5.75 μ m at a -50V bias voltage and 2.39 μ m at a -100V. Despite the expected lower deposition rate of CrN compared to metallic coatings, the thickness observed in the CrN_8h_100V

sample is inconsistent with the expected outcomes. This suggests a potential issue during deposition or when breaking the silicon wafer to obtain cross-sectional images in the SEM.

Comparing the Cr+CrN results, samples coated for 6 hours showed a total thickness of 6.18 μ m at -50V, with 1.38 μ m of CrN, and a total thickness of 5.32 μ m at -100V, with a CrN layer of 0.9 μ m. In contrast, samples coated for 4 hours had total thicknesses of 4.35 μ m at -50V and 3.91 μ m at -100V, with CrN top layers of 0.72 μ m and 0.64 μ m, respectively. This comparison provides a comprehensive understanding of the effects of different coating durations and bias voltages on the CrN coating. On average, the deposition rate for the CrN coating is approximately 0.7 μ m/h at -50V and 0.5 μ m/h at -100V.

Moreover, all coatings exhibit a columnar structure typical of CrN coatings^{212,214–}²¹⁶, with vertically oriented and densely packed structure extending across the entire thickness of the coatings.

Both CrN coatings deposited for 8 hours have a less uniform appearance with some irregular grain shapes. This irregularity may be an inherent characteristic of the film or could result from an irregular break of the silicon wafer, which has affected the film.

The Cr+CrN coatings display a darker colour relative to the upper CrN layer, which clearly distinguishes the interface between the Cr base layer and the upper CrN layer, as indicated by the red line in Figure 99 (c), (d), (e), and (f). The initial chromium layer exhibits a columnar structure that transitions smoothly into the CrN coating. Additionally, the vertically oriented grains are dense and compact. There is no significant difference between -50V and -100V bias voltages, except for a decrease in deposition rate with increasing bias voltage.

Figure 100 shows the XRD graph of the CrN films deposited for 8h at -50 and -100 bias, Cr+CrN films deposited for 6h at -50 and -100 bias, and Cr+CrN films deposited for 4h at -50 and -100 bias.

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Figure 100 – X-Ray spectra the CrN films deposited for 8h at -50 and -100 bias, Cr+CrN films deposited for 6h at -50 and -100 bias, and Cr+CrN films deposited for 4h at -50 and -100 bias.

All the samples exhibit three characteristic peaks of the fcc structure of CrN, found at 37.2° , 43.7° , and 63.5° , corresponding to the (111), (200), and (220) planes. Additionally, the Cr3h-CrN1h samples deposited at -50V and -100V bias voltages show an extra peak around 44.3° , likely originating from the chromium underlayer, as these CrN layers are relatively thin, with less than 0.7 µm.

Overall, the observed diffraction peaks confirm the presence of the expected fcc CrN structure across all samples. The additional peak in the Cr3h-CrN1h samples suggests the influence of the chromium underlayer, particularly in thinner CrN coatings.

Table 25 presents the hardness, elastic modulus, and H/E ratio of the CrN_8h, Cr_4h_CrN_2h, and Cr_3h_CrN_1h samples coated at -50V and -100V bias voltage.

Sample	Hardness (GPa)	Elastic modulus (GPa)	H/E ratio
CrN_8h_50V	20.0 ± 5.7	292 ± 66	0.068
CrN_8h_100V	19.5 ± 5.3	319 ± 73	0.061
Cr4h-CrN2h_50V	20.7 ± 5.1	295 ± 61	0.070
Cr4h-CrN2h_100V	22.9 ± 4.2	301 ± 47	0.076
Cr3h-CrN 1h_50V	12.9 ± 3.8	260 ± 51	0.050
Cr3h-CrN1h_100V	19.5 ± 2.7	285 ± 29	0.068

Table 25 – Hardness, elastic modulus, and H/E ratio of the CrN_8h, Cr_4h_CrN_2h, and Cr_3h_CrN_1h samples coated at -50V and -100V bias

The nano-hardness results for the CrN and Cr+CrN coatings revealed very high values compared with the Cr-coatings showed in the chapter 8 and 9, about 20 GPa. The only exception was the Cr_3h_CrN_1h_50V sample, which presented a similar hardness to the hardest Cr coatings (6h and -50V) around 12GPa. Therefore, the CrN significantly increased the hardness of the coatings compared to the Cr-coatings shown in Chapter 9.

There were no significant differences among the CrN and Cr+CrN coatings regarding the elasticity modulus; the results fluctuated between 260 and 319 GPa.

The CrN and Cr+CrN coatings exhibit higher H/E ratios compared to the Cr coatings, suggesting a potential for higher wear resistance. The Cr4h-CrN2h_100V coating shows the highest H/E ratio at 0.076 GPa, while the Cr3h-CrN 1h_50V has the lowest at 0.05.

Regarding the H/E ratio, the -50V bias voltage coating presented the highest value, and the other coatings fluctuated around a similar ratio.

9.4 CrN wettability

As previously discussed, surface wettability is crucial for predicting surface bubble behaviour and improving boiling efficiency. In chapter 6, we observed that the contact angle of the Cr-coated surface could not be manipulated by adjusting the roughness. Additionally, the chromium coatings exhibited a higher contact angle than the substrate (around 105°), which is not ideal. Therefore, we aim to test whether a thin CrN top layer can decrease or maintain a contact angle similar to the original substrate.

Table 26 presents the contact angle results for the original substrate (ZIRLOTM) and various configurations of Cr+CrN coatings. It should be noted that none of the substrates used in this experiment were previously polished; they were used in their as-received condition.

Samples ID	Contact angle (°)
ZIRLO™	81.65 ± 4.6
CrN_8h_50V	98.69 ± 2.6
CrN_8h_100V	106.2 ± 0.4
Cr4h-CrN2h_50V	100.57 ± 2.8
Cr4h-CrN2h_100V	104.90 ± 2.9
Cr3h-CrN 1h_50V	106.9 ± 3.8
Cr3h-CrN 1h_100V	105.61 ± 0.5

Table 26 – Contact angle results of the uncoated substrate, CrN_8h, Cr_4h_CrN_2h, and Cr_3h_CrN_1h samples coated at -50V and -100V bias

The CrN coating presented contact angles between 98° and 106°, which is higher than ZIRLOTM. The CrN_8h_50V coating exhibited the lowest contact angle among the coatings but was still nearly 20° higher than the substrate value. Meanwhile, the other CrN and Cr+CrN coatings presented contact angles higher than 100°. Neither the fully CrN coatings nor the Cr+CrN combinations were able to decrease the contact angle values. Therefore, the CrN coatings did not improve wettability, as the chromium coatings tested previously.
Similar results were found in the literature which also involved Cr/CrN multilayer coating. It was reported contact angles between 94° and 104 °for the Cr/CrN multilayer coatings²¹⁷.

9.5 Mechanical properties assessments

Figure 101 displays a bar graph (a) with the wear rate calculated based on the average of three wear tests for each sample and load used, and a line chart (b) illustrating wear depth vs. the load for the CrN_8h, Cr_4h_CrN_2h, and Cr_3h_CrN_1h samples coated at -50V and -100V bias voltage.



Figure 101 – (a) Wear rate and (b) wear depth of the uncoated ZIRLO[™], of CrN_8h, Cr_4h_CrN_2h, and Cr_3h_CrN_1h samples coated at -50V and -100V bias voltage.

The CrN_8h_50V presented excellent protection with zero wear rate across all loads. Even though the CrN_8h_100V showed a thinner coating than expected, it exhibits low wear rates of 0.5 mm³/N.m at 4N and 0.7 mm³/N.m at 5N. However, the wear damage reached the substrate at 4 and 5N, probably because of the low thickness.

The samples labelled Cr_4h_CrN_2h exhibited good results under both bias voltages. Friction tests demonstrated a zero wear rate at 3 and 4N, but samples with -50V and -100V presented a minimal wear rate of 0.1 and 0.4 mm³/N·m. As a result, these samples demonstrated a wear depth of 0.8 and 2.7 µm for -50V and -100V bias voltage, which did not penetrate the substrate. The Cr_4h_CrN_2h_50V sample exhibited a higher wear rate but a lower wear depth compared to the Cr_4h_CrN_2h_100V sample because the wear extended more laterally than deeper into the material. This resulted in a significantly larger worn area of 1.6 × 10⁶ µm². In contrast, the Cr_4h_CrN_2h_100V sample had approximately three times the wear depth, but the worn area was only 0.86 × 10⁶ µm².

Conversely, the Cr_3h_CrN_1h coatings at -50V and -100V bias voltages exhibited the poorest performance among the samples. The Cr_3h_CrN_1h_50V coating maintained a good wear resistance up to 4, but it showed a wear rate of 1.7 mm³/N·m at 5N, resulting in a wear depth of 26 μ m, which extended into the substrate. In comparison, the Cr_3h_CrN_1h_100V coating presented no wear protection at any load, and the penetration wear depth was higher than the coating thickness for the three loads tested.

Overall, among all the samples involving CrN in this section, the CrN 8h coating at -50V presented the ideal result with no wear at the highest load 5N.

In this specific case, the expected directly proportional correlation between the H/E ratio and the wear results for the CrN coatings was not observed. For instance, the Cr_3h_CrN_1h_100V coating exhibits the poorest wear resistance, with the highest wear rate and depth. Despite this, the same film demonstrates a high hardness of 19.5 GPa and does not have the lowest H/E ratio. Conversely, the Cr_3h_CrN_1h_50V coating, which performs better than the Cr_3h_CrN_1h_100V, shows the lowest hardness and H/E ratio.

Furthermore, the CrN_8h_50V sample, which provides the best wear protection among these samples, possesses an excellent hardness of 20 GPa but not the highest H/E ratio of 0.068. On the other hand, the sample Cr4h-CrN1h_100V with the highest hardness and H/E ratio presented an acceptable result, exhibiting a low wear rate of 0.04 at 5N and no wear at lower loads. However, it is not the best-performing sample in the group.

Figure 102, Figure 103, and Figure 104 presents the surface 3D morphology of the wear tracks of the CrN_8h, Cr_4h_CrN_2h, and Cr_3h_CrN_1h samples coated at -50V and -100V bias voltage.



Figure 102 – Surface 3D morphology of CrN_8h samples at -50V and -100V bias voltage.



Figure 103 – Surface 3D morphology of Cr_4h_CrN_2h samples at -50V and -100V bias voltage.



Figure 104 – Surface 3D morphology of Cr_3h_CrN_1h samples at -50V and - 100V bias voltage.

The Figure 105 shows an SEM image at 50x magnification along with the EDX mapping, providing an overview analyse on wear track of CrN_8h, Cr_4h_CrN_2h, and Cr_3h_CrN_1h samples coated at -50V and -100V bias voltage.



Figure 105 – EDX mapping (50x) of the wear track of CrN_8h, Cr_4h_CrN_2h, and Cr_3h_CrN_1h samples coated at -50V and -100V bias voltage.

The WLI images clearly illustrate the wear damage caused by the friction test. Additionally, the EDX mapping results confirm that the substrate was reached under the most aggressive load, 5N. Moreover, in some WLI images where no damage was caused, we can see a step up over the wear track; it looks like an accumulation of material. On the EDX mapping, oxygen was found on the wear track, which suggests that an oxide layer was formed and can be observed on the WLP image.

Table 27 compares the friction test results at 5N of the Cr coatings, CrN, and Cr+CrN coatings deposited at –50V and -100V bias voltage.

5N				
Sample ID	Cr coating thickness (μm)	Wear depth (µm)	Wear Rate (mm ³ /Nm)	
Uncoated Zr	-	32.9	121.3	
Cr_50V_4h	5.1 ± 0.1	27.7	4.4	
Cr_3h_CrN_1h_50V	4.4 ± 0.02	26.0	1.7	
Cr_100V_4h	4.7 ± 0.2	30.0	2.2	
Cr_3h_CrN_1h_100V	3.9 ± 0.02	26.2	4.5	
Cr_50V_6h	6.8 ± 0.1	0.0	0.0	
Cr_4h_CrN_2h_50V	6.2 ± 0.06	0.8	0.1	
Cr_100V_6h	6.3 ± 0.4	14.9	0.9	
Cr_4h_CrN_2h_100V	5.3 ± 0.02	2.7	0.04	
Cr_50V_8h	8.7 ± 0.1	0.0	0.0	
CrN_8h_50V	5.8 ± 0.1	0.0	0.0	
Cr_100V_8h	7.5 ± 0.1	3.8	0.2	
CrN_8h_100V	2.4 ± 0.2	0.7	9.3	

Table 27 – Friction test results at 5N of the Cr coatings and CrN coatings or overlayers deposited at –50V and -100V bias voltage.

The effect of the CrN for each coating time can be noticed compared with the Cr coatings of chapter 7. First, all coatings offered at least minimal protection to the substrate; even the poorest results presented a slightly lower wear depth and a significant drop in the wear rate.

Next, the 1h deposition of CrN on the top of 3h Cr deposition showed no significant improvement in wear results in comparison to the Cr coatings deposited for 4h, for both bias voltages. Additionally, no improvements are observed for the sample Cr_4h_CrN_2h_50V compared to the Cr_50V_6h coatings. However, the coating Cr_4h_CrN_2h_100V presented a significant improvement compared to the

Cr_100V_6h, dropping the wear depth from 14.9 to 2.7 μ m and the wear rate from 0.9 to 0.04 mm³/N·m, respectively.

Finally, the 8h coatings of Cr and CrN demonstrated excellent results for the deposition as -50V with no wear at 5N. The CrN_8h_100V coating improved the wear depth, but the wear rate was significantly higher. It is important to note that the CrN_8h_100V, in particular, presented a lower thickness than expected, which might interfere with the final wear results, even though it presented reasonable wear protection under the conditions tested.

Figure 106 shows an SEM image at 100x magnification providing an overview analyse and a zoom at 1kx magnification into the wear track of CrN_8h, Cr_4h_CrN_2h, and Cr_3h_CrN_1h samples coated at -50V and -100V bias voltage.



Figure 106 – SEM images of the wear track of the 5N test of CrN_8h, Cr_4h_CrN_2h, and Cr_3h_CrN_1h samples coated at -50V and -100V bias voltage.

Figure 107 presents EDX maps at 1kx magnification inside the wear track of CrN_8h, Cr_4h_CrN_2h, and Cr_3h_CrN_1h samples coated at -50V and -100V bias voltage.



Figure 107 – SEM images (1kx) inside the wear track of CrN_8h, Cr_4h_CrN_2h, and Cr_3h_CrN_1h samples coated at -50V and -100V bias voltage.

The SEM images of the samples CrN_8h_100V, Cr_3h_CrN_1h_50V, and Cr_3h_CrN_1h_100V, where the substrate was reached, clearly reveal the appearance of the zirconium by a change in contrast observed in the centre of the wear tracks, which is also confirmed in the EDX mapping. Additionally, on the wear

tracks of these samples, we observe debris accumulation characterizing adhesive wear. According to the EDX mapping, the debris accumulates as iron from the counterbody. The arrows in the SEM images indicate some parallel grooves at the coating surfaces along the friction direction (vertical), which could be identified as abrasive wear. According to the EDX mapping, the debris accumulates as iron from the counterbody.

On the other hand, the Cr 4h CrN 2h 50V and Cr 4h CrN 2h 100V samples exhibited minimal wear, leaving only a few marks on the coating surface. The SEM images show black arrows indicating minimal debris accumulation, identified as Fe in the adhesive wear EDX mapping, suggesting in both samples. The Cr 4h CrN 2h 100V sample also showed some tiny grooves in the friction direction, indicating potential abrasive wear in some coating regions. As previously discussed, this last sample experienced deeper wear than the Cr 4h CrN 2h 50V sample. The presence of deeper grooves may account for the greater wear depth observed in the results.

Finally, the CrN_8h_50V sample stands out for its exceptional performance, exhibiting no signs of wear among the samples discussed in this chapter. The minimal debris accumulation from the counterbody and the absence of severe wear as expected underscore its superior wear resistance.

Vickers indentation is commonly used to compare the toughness and analyse crack propagation in hard coatings and thin films due to its simplicity. To assess the damage resistance of the samples, SEM images of the deformation caused by the indentation were captured and are shown in Figure 108.



Figure 108 – Vickers test on of the CrN_8h, Cr_4h_CrN_2h, and Cr_3h_CrN_1h samples coated at -50V and -100V bias voltage.

All samples exhibited severe cracks in the central area of the indented surface, with most of them exposing the substrate, identifiable by the lowest contrast in the centre of the indenter (shown by black arrows). Additionally, all coatings in this section displayed edge cracks around the indentation, indicated by black arrows. The samples with a -50V bias ((a), (c), and (e)) showed more cracks compared to those with a -100V bias ((b), (d), and (f)). The Cr4h-CrN2h_100V coating appeared to have the fewest cracks and a smoother appearance and was the only one without substrate exposure. Overall, these coatings demonstrated poor damage resistance, which may

be attributed to the hard, brittle nature of CrN and poor adhesion strength to the substrate.

Guan *et al.* also utilized Vickers indentation to compare four types of multilayer coatings composed of different metal/ceramic systems⁵⁶. Their coatings were produced using a multi-arc ion plating system, with a bias voltage of -20V for metallic layers and -25V for ceramic layers. The material combinations studied were Cr/CrN, Cr/ZrN, Zr/CrN, and Zr/ZrN multilayer coatings, each consisting of 15 layers with a total thickness ranging from 5 to 7 μ m. The Cr/CrN coating exhibited results similar to those observed in this work. SEM images of the Vickers indentation revealed significant crack propagation at the centre of the indentation, with radial cracks extending outward. Guan *et al.* reported that the Zr/ZrN multilayer coatings tested in Chapter 9 of this work, particularly the Cr_6h_100V and Cr_8h_150V samples, demonstrated superior damage resistance compared to the CrN coatings discussed in this chapter.

Figure 109, Figure 110, Figure 111, Figure 112, Figure 113, and Figure 114 presents the SEM images of the scratch tracks, and the representative curves of acoustic emission signal and penetration depth as a function of the applied normal CrN 8h 50V, load obtained in the scratch test for CrN 8h 100V, Cr 4h CrN 2h 50V, Cr_4h_CrN_2h_100V, Cr_3h_CrN_1h_50V, and Cr 3h CrN 1h 100V samples, respectively.

The scratch test curves also present the first and the second critical loads denominated as Lc1 and Lc2, respectively. Lc1 and Lc2 are the critical loads estimated from the scratch test, they can be used to determine the cohesive strength and interfacial adhesive strength of the coating, respectively. Lc1 defines the lower critical load corresponding to cracking. It is possible to determine the location of Lc1 by a sudden increase in the acoustic emission spectrum for a normal. On the other hand, Lc2 defines the upper critical load characterised by continuous substrate exposure²¹¹.



Figure 109 – SEM image of the scratch track, and the representative curves of acoustic emission signal and penetration depth obtained in the scratch test of CrN_8h_50V sample.



Figure 110 – SEM image of the scratch track, and the representative curves of acoustic emission signal and penetration depth obtained in the scratch test of CrN_8h_100V sample.



Figure 111 – SEM image of the scratch track, and the representative curves of acoustic emission signal and penetration depth obtained in the scratch test of Cr_4h_CrN_2h_50V sample.



Figure 112 – SEM image of the scratch track, and the representative curves of acoustic emission signal and penetration depth obtained in the scratch test of Cr_4h_CrN_2h_100V sample.



Figure 113 – SEM image of the scratch track, and the representative curves of acoustic emission signal and penetration depth obtained in the scratch test of Cr_3h_CrN_1h_50V sample.



Figure 114 – SEM image of the scratch track, and the representative curves of acoustic emission signal and penetration depth obtained in the scratch test of Cr_3h_CrN_1h_100V sample.

The critical loads Lc1 and Lc2 values are shown in Table 28.

Sample	Lc ₁ (N)	Lc ₂ (N)
CrN_8h_50V	7.2	8.8
CrN_8h_100V	6.1	10
Cr4h-CrN2h_50V	4.5	10
Cr4h-CrN2h_100V	1.5	-
Cr3h-CrN 1h_50V	5.5	-
Cr3h-CrN 1h_100V	7.7	-

Table 28 – Critical loads of the scratch test of the CrN_8h, Cr_4h_CrN_2h, and Cr_3h_CrN_1h samples coated at -50V and -100V bias voltage.

The CrN_8h_50V sample exhibited notable peaks in acoustic emission (AE) starting at 7.2 N, identifying the Lc1 location where crack initiation occurs. The penetration depth (PD) increases with the applied load. However, a sudden increase is observed at 8.8 N due to substrate exposure, as confirmed by the SEM image. During the scratch test, the CrN_8h_50V sample showed multiple cracks and several points where the substrate was revealed.

The AE of the CrN_8h_100V coating displayed the first peak at 6.1 N, where cracks appeared at the scratch edges. A second peak at 10 N corresponded with Lc2, where coating failure exposed the substrate. From the Lc2 point onwards, the coating completely delaminated until the end of the scratch. The PD increased with the applied load, indicating progressive penetration into the material.

The Cr4h-CrN2h_50V coating presented a gradual increase in AE from 3 N and fluctuates around 5% until the end of the test. The Lc1 point was observed at 4.5 N with a few cracks on the scratch track, and substrate exposure began around 10 N, indicating the Lc2 point. From Lc2 onwards, the substrate was slightly exposed, however, the substrate experienced severe delamination from around 22 N until the end of the scratch track. The PD showed a steady increase throughout the test.

The Cr4h-CrN2h_100V samples demonstrated severe delamination from the beginning of the scratch test, with Lc1 and Lc2 points occurring simultaneously at 1.5 N. The substrate was visible along the entire wear track. The AE showed a small peak

around 13 N but remained practically stable during the test. Meanwhile, the PD exhibited a progressive increase with the applied load.

Similarly, the Cr3h-CrN1h_50V sample also revealed the substrate at the beginning of the test at 5.5 N, where a small peak in the AE curve was observed. Lc1 and Lc2 coincided at this point, as the initial cracks already exposed the substrate. The PD increased progressively until the end of the test. The substrate was visible along the entire length of the wear track.

Finally, the Cr3h-CrN1h_100V sample showed a small peak in the AE curve at 5.5 N, marking the Lc1 point with cracks and substrate exposure. The substrate was visible along all the scratch tracks. However, around 16 N, the PD curve showed a significant increase, and the SEM image revealed severe delamination extending until the final load of the test at 30 N.

Overall, the CrN and Cr+CrN coatings exhibited poor adhesion to the substrate, as evidenced by severe delamination and cracking observed during the scratch tests. The hard CrN coatings likely fractured due to its brittle nature. Among the samples, the CrN_8h_50V coating demonstrated the lowest substrate exposure under the same load, indicating a potentially stronger bond between the coating and the substrate compared to the other coatings. In contrast, the other samples showed substrate exposure at the test's onset until the scratches end, underscoring their comparatively weaker adhesion properties.

Therefore, the CrN-coatings presented a worse adhesion to the substrate compared to the Cr coatings. In addition, even using an intermediary chromium layer in the Cr+CrN coating, no improvement was noticed in the adhesion to the substrate.

Zhou *et al.* reported similar findings in their scratch tests on multilayer coatings of Cr and CrN. They experimented with alternating $(Cr/CrN)_n$ multilayer coatings, where n represents the number of layers: 3, 6, 12, and 24. The coatings were deposited using magnetron sputtering with a bias voltage of -60V, reaching a total thickness of approximately 5 µm. Their study showed intense delamination and substrate exposure along the entire length of the coatings, corroborating the results presented in this section²¹⁷.

Guan *et al.* also performed scratch tests on a 15-layer coating alternating between Cr and CrN layers. The scratch test images in their study showed that the Cr/CrN coating developed radial cracks and edge delamination as the applied load increased. However, no severe delamination was reported, suggesting that the

multilayer system may perform better than a CrN top layer over a dense chromium layer, as tested in our work⁵⁶.

9.6 Summary

In this chapter, our goal was to explore the potential of chromium nitride (CrN), known for its higher hardness, as an overlayer on chromium (Cr) coatings to enhance wear resistance and wettability. We prepared three sets of samples to facilitate a direct comparison with Cr-coated samples. The first set involved a Cr layer deposited for 3 hours, followed by a 1-hour CrN deposition. The second set consisted of a 4-hour Cr coating combined with a 2-hour CrN overlayer. The third set featured an entire CrN film deposited over 8 hours to assess its performance relative to Cr coatings. Each of these coatings was applied using -50V and -100V bias voltages, resulting in six samples.

In terms of hardness, the CrN and Cr+CrN coatings exhibited significantly higher values, around 20 GPa, compared to the Cr-only samples. However, the sample with a 3-hour Cr coating and 1-hour CrN deposition at -50V bias voltage showed hardness similar to the hardest Cr coating, which was around 12 GPa after 6 hours of deposition at -50V.

In our friction tests, the 8-hours CrN coating demonstrated excellent wear resistance. However, it was challenging to determine the optimal bias voltage due to potential issues with the -100V bias coatings. The Cr+CrN combinations, specifically the 4-hours Cr and 2-hours CrN samples, showed good wear resistance at both bias voltages. Conversely, the samples with a 3-hour Cr and 1-hour CrN coating provided the least protection to the substrate at both -50V and -100V bias voltages.

Therefore, adding a harder CrN layer on top of the Cr coatings did not enhance wear resistance. Although the CrN_8h_50V coating performed as well as the best Cr coating in wear tests (Cr_6h_50V), it has certain drawbacks. Specifically, CrN coatings have a lower deposition rate and require a more complex fabrication processes due to maintaining precise stoichiometry.

Regarding the wear mechanism, SEM and EDX analyses revealed both adhesive and abrasive wear on the CrN and Cr+CrN coated samples. The samples CrN_8h_100V, Cr_3h_CrN_1h_50V, and Cr_3h_CrN_1h_100V, which showed significant wear, exhibited adhesive and abrasive wear. In contrast, the

Cr_4h_CrN_2h_50V and Cr_4h_CrN_2h_100V samples displayed minimal wear, characterized by slight adhesive wear and minor abrasive grooves. Notably, the CrN_8h_50V sample demonstrated superior wear resistance, with minimal debris accumulation and no severe wear, indicating its exceptional performance.

As for wettability, the CrN coatings did not show any improvement compared to the Cr coatings.

The Vickers hardness test revealed that the CrN and Cr+CrN coatings developed cracks and deformations, indicating poor damage resistance and low toughness. Similarly, in scratch tests, the CrN and Cr+CrN coatings exhibited poor adhesion to the substrate, as evidenced by severe delamination and cracking.

In summary, the CrN and Cr+CrN coatings did not significantly improve wear resistance or wettability compared to the Cr-coated samples. Moreover, the CrN-based coatings demonstrated inferior damage resistance, higher toughness, and inferior adhesion to the substrate than the Cr coatings. Consequently, CrN-based coatings are not suitable as a replacement for Cr coatings or as a top layer addition, as they offer no clear advantages to the system.

IV. Synopsis

Chapter 10. Conclusion and future work

This chapter summarizes the main results presented in this thesis and discusses how the objectives outlined in the Introduction section (Chapter 1) were achieved. Additionally, future research projects are suggested based on the results presented in this thesis.

10.1 Overall conclusion and discussion

This thesis aimed to develop a Cr-based coating for zirconium alloy fuel rod cladding using magnetron sputtering, with a primary focus on enhancing mechanical performance and mitigating grid-to-rod fretting (GTRF) during reactor operation. This goal was accomplished by optimizing the deposition parameters for the Cr-based coatings, followed by comprehensive characterization and testing to establish correlations between the coating properties and their performance. The specific objectives were also achieved and are summarised in the sequence.

The first objective of this investigation was to determine the influence of the surface roughness of the underlying Zr alloy substrate on the water contact angle of the Cr-coated samples. This investigation involved the variation of the substrate roughness and subsequently measuring the wettability of the surfaces after applying the Cr-based coatings.

Our studies showed that the Cr coatings preserved the substrate's polished roughness on the coating surface. However, we observed that surface roughness did not significantly affect the contact angle of the Cr-coated samples. Therefore, based on the deposition technique, parameters, and roughness levels used in this work, we conclude that roughness alone cannot be used to manipulate the contact angle of Crcoated surfaces.

Furthermore, our observations indicate that the chromium coating alters the surface properties, favouring hydrophobicity. It appears that other factors influencing wettability, such as surface chemistry, may have a more significant impact than roughness. These findings suggest that the substrate roughness manipulation tested in this study may not be ideal for improving critical heat flux (CHF) performance.

Therefore, we do not recommend modifying the surface roughness of the original nuclear fuel cladding. Introducing an additional polishing step would increase

production costs and extend manufacturing time. Moreover, such an effort yields no significant improvement in surface wettability, further undermining its practicality.

The second goal of this thesis was to produce an ATF cladding with a Cr-based coating and optimized coating parameters by magnetron sputtering. This study was based on the variation of two parameters: bias voltage and deposition time (coating thickness). The main conclusions regarding the Cr-based coatings are summarized below.

Firstly, Cr-coated samples were produced using a 1-hour deposition time across a range of bias voltages, from -50V to -250V, to evaluate how bias voltage affects the deposition rate. An apparent decrease in coating thickness was observed as the bias voltage increased. Preliminary friction and wear tests also showed that wear resistance decreased with higher bias voltages. However, since coating thickness varied with each bias voltage, it was difficult to determine whether the bias voltage or the thinner coatings caused the reduced wear resistance. Based on these results, we conclude that the deposition rate drops significantly with increasing bias voltage due to the re-sputtering effect. Additionally, a deposition time of 1 hour does not result in a coating thick enough to protect the substrate effectively.

Secondly, Cr coatings deposited for 4, 6, and 8 hours at selected bias voltages of -50V, -100V, -150V, and -200V provided further insight into achieving our objectives. Overall, the coatings deposited for 4 hours exhibited the highest deposition rates. For the 6-hour coatings, the wear rate increased with higher bias voltages, while the 8-hour coatings showed a notable improvement in wear resistance across all bias levels. These results indicate that deposition time and lower bias voltages play a role in increasing coating thickness. However, the influence of bias voltage on wear resistance remains unclear, as variations in coating thickness continue to affect the outcomes.

Thirdly, to address this issue, we compared Cr coatings with similar thicknesses of approximately 6 µm, deposited at bias voltages of -50V, -100V, -150V, and no bias applied (NBA). These comparisons demonstrated that bias voltage significantly influences wear resistance, scratch performance, and crack resistance. Based on these results, we identified an optimized combination of bias voltage and coating thickness that enhances the overall performance of the Cr coatings.

In general, the uncoated samples showed the highest wear rate, followed by the Cr-coated samples produced with no applied bias (NBA). The coating deposited at -

50V showed no measurable wear, while those deposited at -100V and -150V exhibited low wear rates. In terms of scratch and crack resistance, the coating produced with a -100V bias performed the best. The poorest performance was observed in the NBA sample, followed by the -50V coating. The -150V coating showed moderate results.

We conclude that all bias voltage coatings provided some level of protection against wear. However, the Cr-coated ZIRLOTM at -50V bias voltage exhibited the best wear resistance due to its higher hardness and smaller grains. However, despite its superior wear resistance, the -50V coating had the lower resistance to cracking and the worse adhesion to the substrate. On the other hand, the -100V coating offered the highest resistance to deformation and adhesion but the worst wear resistance among the biased samples.

Regarding the CrN coatings, the 8-hour CrN coating demonstrated excellent wear resistance. The Cr+CrN combinations, particularly the samples with 4-hour Cr and 2-hour CrN coatings, also showed good wear resistance at both bias voltages. Conversely, the samples with 3-hour Cr and 1-hour CrN coatings provided the least protection to the substrate at both -50V and -100V bias voltages. The Vickers hardness test revealed that all CrN and Cr+CrN coatings developed cracks and deformations, indicating poor damage resistance and low toughness. Similarly, scratch tests showed that CrN and Cr+CrN coatings exhibited poor adhesion to the substrate, as indicated by severe delamination and cracking. Additionally, regarding wettability, CrN coatings did not show any improvement over Cr coatings.

Comparing Cr and CrN coatings, we conclude that CrN did not offer any significant advantages over Cr coatings. Although the fully CrN coating exhibited excellent wear resistance, it was not superior to the Cr coating with a 6-hour deposition time at a -50V bias voltage. It is also important to note that CrN coatings have a lower deposition rate and involve a more complex fabrication process than Cr coatings. Moreover, CrN coatings did not demonstrate improved scratch resistance or reduced cracking. Therefore, the CrN variations tested in this project were unsuitable in terms of crack resistance, scratch behaviour, wettability improvement, or practicality in manufacturing.

In conclusion, this study has demonstrated that chromium (Cr) coatings produced by magnetron sputtering can significantly enhance the mechanical performance of zirconium-based cladding, particularly in terms of wear resistance—a key factor in mitigating grid-to-rod fretting (GTRF) in nuclear reactors. Based on a

comprehensive analysis of the results, the recommended solution is a Cr coating with a minimum thickness of $6 \mu m$, deposited at -50V bias voltage. In contrast, the CrN coatings evaluated in this work did not exhibit any clear advantages over the Cr coatings and are therefore not recommended for further development under the same deposition conditions.

Overall, the research successfully achieved its objective of developing and accessing Cr-based coatings to improve the safety and reliability of accident-tolerant fuel (ATF) for LWR, while also identifying optimal processing parameters and recognizing the limitations of current coating approaches.

10.2 Future work suggestions

As a result of the findings of this thesis, the following suggestions are proposed for future works:

Oxidation tests:

The wear and scratch resistance results obtained for the Cr coatings were promising. However, to comprehensively determine the most suitable coating parameters for implementation in LWRs, these coatings must undergo additional testing, specifically irradiation and oxidation tests. These tests are crucial for assessing the coatings' performance under actual reactor conditions. Therefore, future work should focus on conducting irradiation and oxidation tests to complement the existing results. By integrating these findings, it will be possible to identify the optimal parameters that meet all the necessary requirements for safe and effective use in LWR environments.

Improved the wear test conditions:

In this work, the friction tests were conducted within the limitations of the available equipment and project timeline. For example, the tribometer used in this study was unable to perform a proper fretting wear test due to its minimum amplitude capability of 2 mm, whereas a fretting wear test requires a much smaller amplitude, typically less than 100 μ m. Therefore, future work should prioritize enhancing the wear test conditions to better reflect the internal conditions of LWRs.

First, fretting wear tests should be conducted using equipment capable of small amplitudes to accurately simulate the actual wear conditions experienced by fuel cladding in reactors. Second, wear tests should be performed in a water environment to assess the impact of fluid presence on wear resistance. Third, a heating stage should be integrated into the tribometer to investigate the effect of elevated temperatures on wear behaviour during fretting tests. Finally, future studies should include long-term performance testing of the coatings in an autoclave, subjecting the samples to conditions that closely mimic the operational environment of nuclear reactors, including high temperature, pressure, and radiation.

Wettability and CHF performance improvement:

The findings in this project did not present positive results regarding CHF performance. The Cr and CrN coatings exhibited higher contact angles, and the manipulation of the roughness did not impact the wettability of Cr coatings. Therefore, future works should focus on different strategies to improve surface wettability by decreasing the contact angle in the cladding surface. An alternative option might be a thin top layer of a hydrophilic material that does not compromise the Cr coating performance.

Scale-up studies for industrial application:

Considering the total length of the fuel cladding tubes of 4 m, moving from laboratory-scale experiments to industrial-scale production is essential for practical implementation. Future work should focus on scaling the magnetron sputtering process to larger substrates and more complex geometries, such as full-scale fuel cladding rods.

Chapter 11. References

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