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Characterization and Corrosion Performance of Chromium-Based Bilayer Coatings for Lead-Cooled Fast Reactors

TESI DI LAUREA MAGISTRALE IN
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Abstract

Lead-Cooled Fast Reactors (LFRs) are recognized as a pivotal technology for the future of sustainable and safe nuclear power generation. However, commercial LFR deployment is currently hindered by severe material degradation induced by the heavy liquid metal coolant. Applying protective coatings has emerged as the primary near-term mitigation strategy. Chromium-based coatings are particularly promising due to their ability to spontaneously form a passivating chromia (Cr_2O_3) scale.

This thesis, conducted by the NanoLab research group at Politecnico di Milano in collaboration with *newcleo*, aims to evaluate the viability of HiPIMS-deposited chromium as a protective barrier for LFRs. The work focuses on two core objectives: understanding the oxidation behavior of the metallic films and assessing their corrosion performance in liquid lead. To achieve these, the study systematically characterizes the high-temperature structural evolution of the chromium layers to optimize thermal oxidation parameters and evaluates the degradation mechanisms of the resulting bilayer architectures under LFR-relevant conditions.

Experimental findings proved the successful growth of dense, continuous, and compressively stressed Cr_2O_3 scales via controlled thermal annealing. Subsequently, two optimized coatings were tested in LFR-relevant liquid lead, revealing a stark divergence in their protective performances. In contrast to the extensive lead penetration observed in the sample annealed at 600°C for 5 h, the 600°C-10h annealed coating appeared to resist macroscopic infiltration and largely kept its structural integrity, though it could not completely prevent outward elemental diffusion. This divergence points to a potential correlation between the initial defectivity of the grown oxide and its anticorrosive capabilities. Ultimately, although the 10 h coating provided improved corrosion resistance, both configurations exhibited interfacial delamination at the chromium-steel interface.

These findings highlight the importance of optimizing the pre-exposure oxide microstructure for improving the corrosion resistance of chromium-based coatings in liquid lead, while also emphasizing the need to enhance coating adhesion.

Keywords: Lead-Cooled Fast Reactors, Liquid Metal Corrosion, Chromium Coatings, HiPIMS, Chromia, Thermal Oxidation, Thin Films

Abstract in lingua italiana

I reattori veloci raffreddati a piombo (LFR) rappresentano una tecnologia cruciale per la futura produzione di energia nucleare sicura e sostenibile. Tuttavia, il loro impiego commerciale è attualmente limitato dal grave degrado dei materiali indotto dal refrigerante metallico liquido. L'applicazione di rivestimenti protettivi è emersa come la principale strategia di mitigazione a breve termine. I rivestimenti a base di cromo risultano particolarmente promettenti grazie alla loro capacità di formare spontaneamente uno strato passivante di ossido di cromo (Cr_2O_3).

Questa tesi, svolta dal gruppo di ricerca NanoLab del Politecnico di Milano in collaborazione con *newcleo*, mira a valutare l'efficacia del cromo depositato tramite HiPIMS come barriera protettiva per gli LFR. Il lavoro si focalizza su due obiettivi principali: comprendere il comportamento ossidativo dei film metallici e valutarne le prestazioni in condizioni di corrosione in piombo liquido. A tal fine, lo studio caratterizza l'evoluzione strutturale dei film di cromo quando esposti ad ambienti ossidanti ad alta temperatura, al fine di ottimizzare i parametri di ossidazione termica, valutandone poi le proprietà anticorrosive quando esposti a piombo liquido ad alta temperatura.

I risultati sperimentali hanno confermato la potenzialità del trattamento di ossidazione controllata per accrescere strati di Cr_2O_3 densi, continui e in stato di compressione. Due rivestimenti ottimizzati sono poi stati testati in piombo liquido, rivelando una marcata differenza nelle prestazioni. A differenza del campione trattato a 600°C per 5 ore, che ha mostrato un'estesa penetrazione del piombo, il rivestimento ossidato per 10 ore a 600°C ha resistito all'infiltrazione macroscopica, mantenendo l'integrità strutturale, pur non impedendo la diffusione esterna degli elementi del substrato. Tale divergenza suggerisce una correlazione tra la difettività iniziale dell'ossido e la sua performance. Infine, entrambi i campioni hanno subito delaminazione all'interfaccia tra cromo e acciaio.

Tali evidenze sottolineano l'importanza di ottimizzare la microstruttura dell'ossido pre-esposizione per migliorarne la resistenza alla corrosione, evidenziando al contempo la necessità di incrementarne l'adesione al substrato.

Parole chiave: Reattori veloci raffreddati a piombo, Corrosione da metallo liquido, Rivestimenti al cromo, HiPIMS, Ossido di cromo, Ossidazione termica, Film sottili

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Part I

The Challenges of Nuclear Power Production

1 | Nuclear Energy

This chapter provides a comprehensive foundation for the subsequent experimental work by tracing the evolution of nuclear energy from its fundamental physical principles to the forefront of modern reactor design. It begins with an overview of the nuclear fission process and its historical deployment, emphasizing the critical role of atomic power in addressing contemporary global decarbonization and energy security targets. Subsequently, the progressive development of reactor generations is examined. By highlighting the vulnerabilities of conventional designs, the discussion ultimately establishes the driving motivations behind the transition towards Accident Tolerant Fuels and advanced Generation IV systems.

1.1. Nuclear Fission

Nuclear fission is the nuclear process in which a heavy nucleus is split apart, generating fission products. This reaction can be either spontaneous (as in the case of Californium-252) or artificially induced. It is possible, for certain nuclei, to induce the absorption of a neutron to trigger the fission event: the configuration of the system after the absorption event is very unstable, leading to a natural evolution toward the fragmentation into fission products. The elements for which this process is likely to occur with thermal neutrons are called fissile (Uranium-235, Plutonium-239). If a fast neutron is required to trigger the reaction, the element is referred to as fissionable (Uranium-238, Thorium-232) [1]. When the nucleus splits apart, it typically produces two lighter nuclei (fission fragments), several neutrons and, most importantly, energy (200 MeV per fission event, for U_{235}). This comes in the form of kinetic energy of the products, which, in a reactor, is then converted into thermal energy within the fuel; this heat is what nuclear power plants are designed to ultimately convert into electricity. In Figure 1.1 the specific case of U_{235} is illustrated.

Figure 1.1a schematizes the fission process of U_{235} . Indeed, fission, like any other nuclear reaction, is governed by probability; the fission fragments vary stochastically, resulting in the mass distribution illustrated in Figure 1.1b [1].

Nuclear reactors work thanks to the fission chain reaction: a self-sustained process in

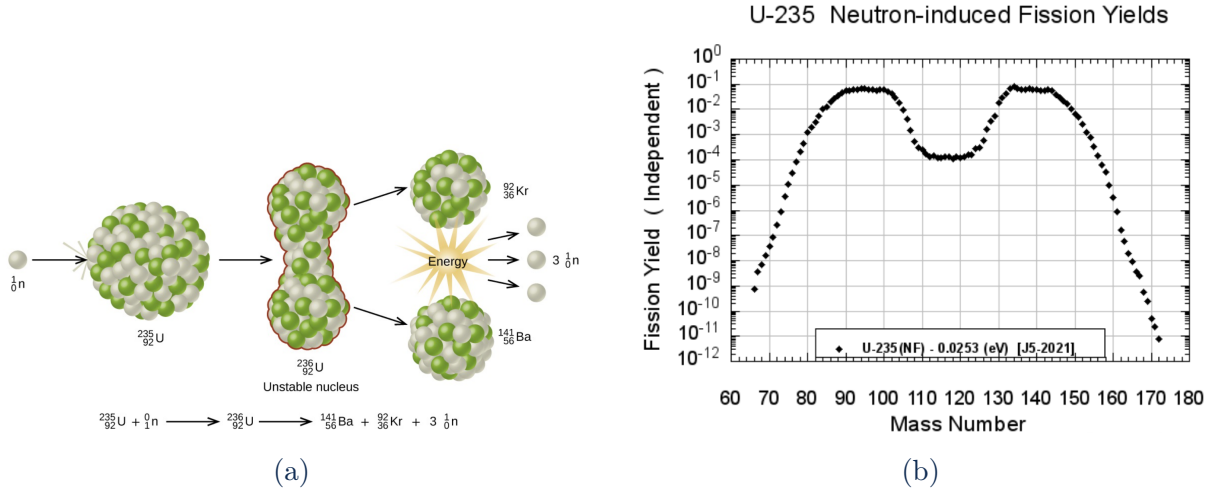


Figure 1.1: Scheme of the (a) fission process and (b) fission yield associated to Uranium 235.

which the neutrons required to trigger fission events are the products of previous ones. The fuel is typically manufactured in the form of pellets, small cylindrical elements housed within fuel rods. These rods are inserted into the reactor's core, where a flowing coolant removes the generated heat to power a Rankine cycle where electricity is generated through a steam turbine. Based on this fundamental concept, many designs have been developed in an effort to exploit atomic energy as efficiently as possible. This immense undertaking has presented significant engineering challenges and, subsequently, led to major technological progress. A brief overview of the development of the nuclear industry will be provided in the following sections.

1.2. Evolution and Current Status of the Nuclear Industry

The first nuclear reactions were observed at the beginning of the 20th century, and, with the development of nuclear physics in the following decades, a new era was about to begin. Nuclear fission was first achieved in 1938 by two German physicists, Otto Hahn and Fritz Strassmann. This scientific breakthrough led to the launch of the Manhattan Project in 1939, which, while resulting in the tragic events of World War II, paved the way for the civilian application of nuclear energy in the post-war era. In 1954, the first-ever power plant was connected to the Soviet grid in Obninsk. From that moment on, nuclear power production was introduced into the energy mix of many countries [2].

Nowadays more than ever, the necessity for modern countries to construct a reliable,

secure, and sustainable energy supply chain is under the spotlight of political debate. Nuclear energy is considered one of the most important players when considering the urgency for the world to decarbonize the energy sector. As mentioned, among others, by the International Energy Agency (IEA) [3], boosting the global nuclear installed power is mandatory if the "Net Zero Emissions" condition is to be met by 2050. Indeed, nuclear reactors offer a virtually carbon-free electricity source with life-cycle emissions as low as 5 g CO_2 eq./kWh [4]. In addition, Atomic power guarantees minimal land use, thanks mainly to the enormous energy density of uranium [4].

Beyond its low carbon footprint, this energy source takes a key role in the improvement of national energy security and strategic autonomy. Indeed, concerning the employment of critical raw materials, nuclear energy is a superior solution compared, especially, to photovoltaics [4]. Furthermore, the supply chain of uranium ore is considered significantly more reliable than that of hydrocarbons. Notably, the largest uranium reserves are located in geopolitically stable areas, such as Canada and Australia [5]. The risk of supply disruptions is further mitigated and potentially eliminated by the advent of next-generation reactors. Fast breeder reactors are designed to operate with a closed fuel cycle, guaranteeing long-term energy sustainability and low radioactive waste production [6].

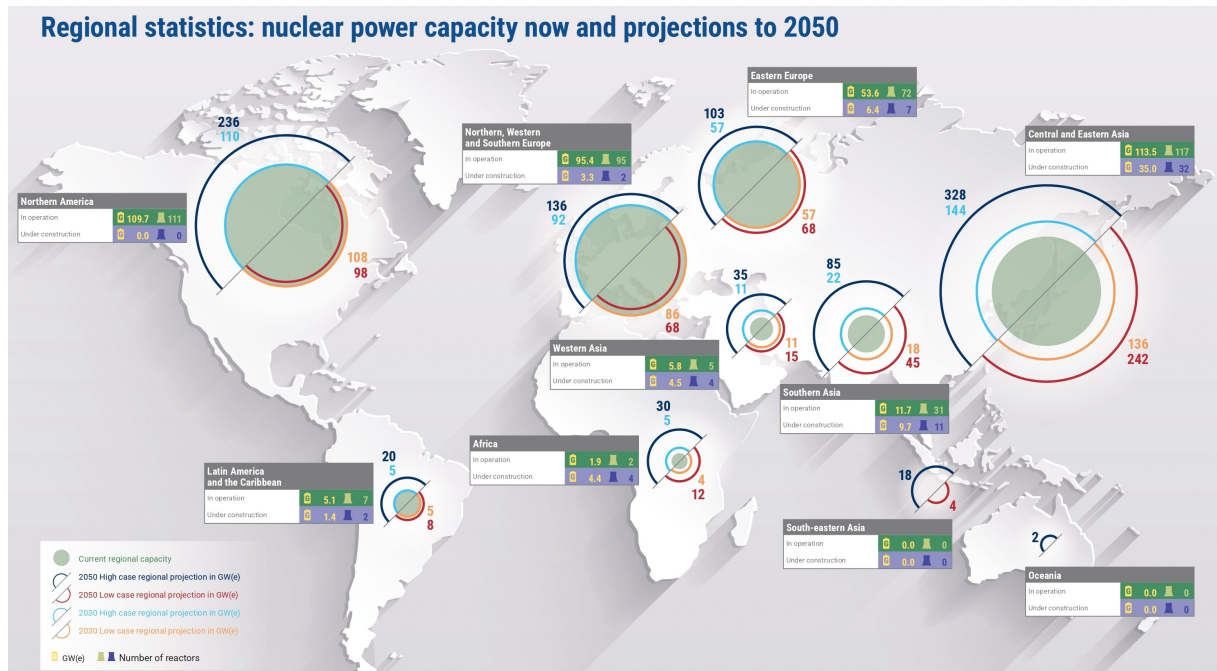


Figure 1.2: World Nuclear power status: geographic distribution of existing and under construction plants. The projections of installed power to 2030 and 2050 are reported, according to the International Atomic Energy Agency (IAEA) report [7].

Regarding the present deployment of nuclear energy, globally, 413 reactors are in operation

and 69 are under construction [7]. With almost 400 GWe of net installed power, fission reactors satisfy 10% of the global electricity demand. In 2023, at COP28, the "Declaration to Triple Nuclear Energy by 2050" was signed; at present, 38 countries (Italy included) have embraced the cause, emphasizing the credibility of nuclear energy in the decarbonisation process [8, 9]. As visible in Figure 1.2, the fleet of nuclear reactors is expected to grow massively in the next decades, including in the Western countries where, barring France (whose nationalized nuclear program launched in the 70s was never abandoned), the share of electricity coming from nuclear has decreased significantly over the last thirty years [10].

1.3. Current Generations of Nuclear Reactors

In 2000, the US Department of Energy proposed a categorization of the existing reactor designs in Generations (schematized in Figure 1.3), to define a general framework for the current and future technologies [6]. Generation I includes the first prototypes, developed as demonstrators for the feasibility of civilian nuclear. They were built in the 1950s and 1960s, and they operated at power levels that were "proof-of-concept", just a few of them had a commercial aim. A peculiar example was the Magnox reactor located at the Wylfa Nuclear Power Station in Wales, which remained attached to the grid until 2015, after more than 40 years of power production [11].

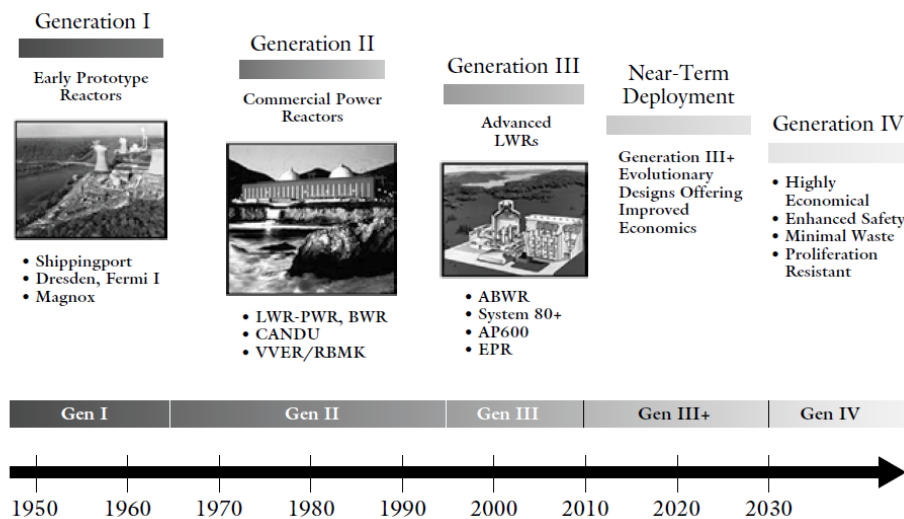


Figure 1.3: Generations of nuclear power with principal reactor models. Figure adapted from [11].

Generation II comprises the bulk of the 400+ commercial Pressurized Water Reactors (PWR) and Boiling Water Reactors (BWR). In addition, also Advanced Gas Reactors

(AGR), CANada Deuterium Uranium reactors (CANDU) and Vodo-Vodyanoi Energeticheskyy Reactors (VVER) are included in Generation II. These designs aimed at producing reliable and economical electricity, with operational lifetime of 40+ years. They use traditional active safety systems. Most of the Gen II plants still in operation in the West were manufactured by one of three companies: Westinghouse, Framatome, and General Electric [11].

Generation III/III+ reactors are essentially the direct evolution of Gen II, with improved efficiency, fuel usage and, crucially, passive safety systems. Reactors of this category were built in Olkiluoto (Finland), Flamanville (France), Georgia (USA), Russia and China. The deployment of these reactors in Western countries was severely hindered by significant economic hurdles and protracted construction delays. Conversely, in Eastern nations, numerous units were completed with notable success. This divergence underscores the cause of the Western economic struggles: Generation III plants were initiated after decades of stagnation in the nuclear sector. The industry faced a difficult restart, struggling against the atrophy of the entire supply chain and a depleted specialized workforce [11].

1.3.1. Safety Implications of the Fukushima-Daiichi Event

In 2011 the major accident occurred in Japan highlighted the necessity of strong updates in the design of fission power plants. In March 2011, Japan experienced one of the worst tsunamis in its history. The flooding of the Fukushima nuclear power plant (NPP) caused serious damage to the six BWR units hosted in the facility, resulting in severe radiological contamination of the surrounding area. Even though no radiation-induced deaths have been officially detected, the evolution of the event underscored the critical vulnerabilities of Gen II reactors [12]. Primarily, these designs were equipped with insufficient passive cooling safety systems, which failed under the extreme conditions stemming from the tsunami [12]. Furthermore, the disaster brought to light another significant challenge inherent to LWRs: oxidation of Zircaloy. When this special alloy reaches temperatures above 1200°C, a strongly exothermic and autocatalytic oxidation reaction is triggered, leading to heavy heat production and explosive hydrogen release [12].

The events of Fukushima exposed the critical vulnerabilities of current LWR fuel system design and refocused international research efforts to develop Accident Tolerant Fuels (ATF) with increased safety margins [13]. ATF concepts represent a paradigm shift towards enhancement of accident tolerance of nuclear fuel, improving the coping time during severe accidents. The most widely accepted solutions to reach such a goal aim to improve existing technologies using coatings made of materials which have already been

used in nuclear industry, like chromium [13]. This approach guarantees minimal effects on normal operations and potential for rapid licensing and deployment.

Furthermore, what occurred in Japan marked a major turning point for the development of next generation reactors: the nuclear community realized that improvements to existing water-cooled designs might not be enough to restore public confidence. This catalyzed a renewed interest in Generation IV systems. These advanced reactors are considered as the future of nuclear power generation, offering inherent and passive safety features, enhanced resource utilization, and the critical capability to close the nuclear fuel cycle [6].

1.4. Generation IV Reactors

The fourth Generation comprises those advanced reactors intended to serve as a reliable source of baseload power while addressing the key challenges of operating through a closed fuel cycle, guaranteeing inherent safety features with low amount of radioactive production and high thermal efficiency [14]. These concepts are candidates for the realization of both large scale power plants and Small Modular Reactors (SMRs). The international development of these reactors is coordinated by Generation IV International Forum (GIF), which in 2002 identified the six designs reported in Figure 1.4 as the most promising ones to be deployed within 2050 [6].

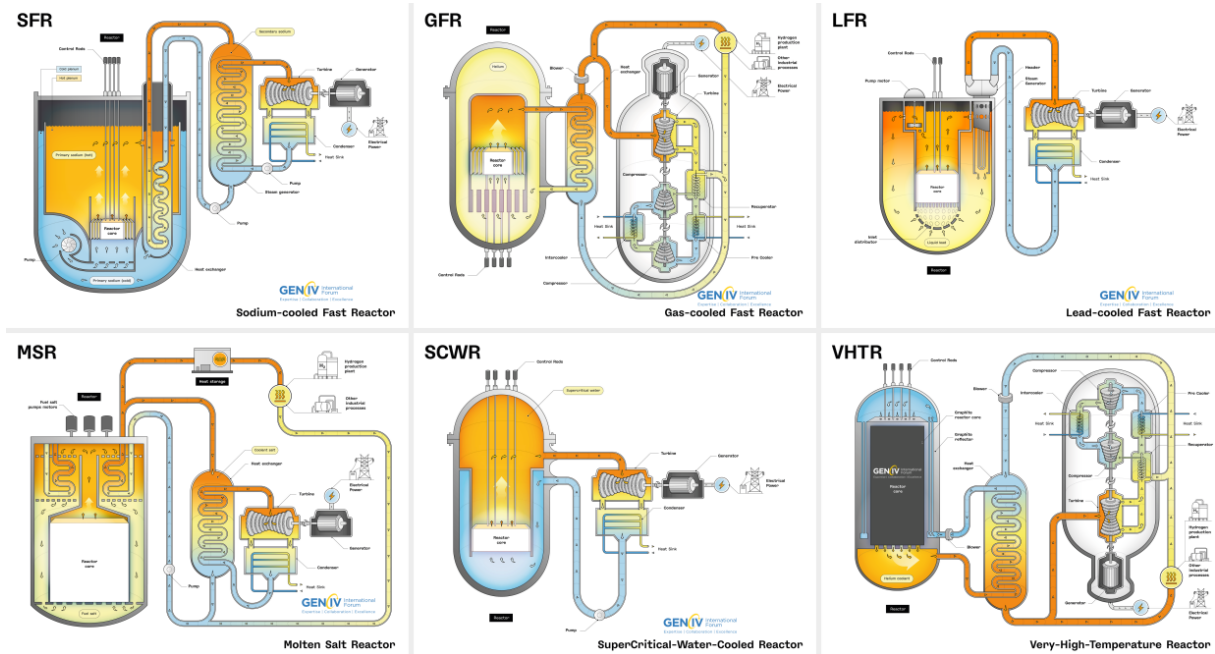


Figure 1.4: Plant conceptual design of the six Generation IV reactors [6]

It must be specified that none of the designs belonging to Gen IV has reached large scale commercialization yet. However the massive research efforts of the last decades lead to significant achievements. The most mature technologies are Sodium Cooled Fast Reactors (SFR), Very High Temperature Gas Reactors (VHTGR) and Lead Cooled Fast Reactors (LFR). Prototypes SFRs were operated in France during the second half of 20th century (Phénix and Superphénix), whereas nowadays Russia and China are already operating commercial SFRs; VHTGRs represent another mature technology, exploitable also as a heat source for high temperature industrial processes. LFRs have been operated for decades for USSR submarines propulsion, nowadays Russia is building a pilot reactor (BREST-OD-300). In Europe, China and USA multiple projects are ongoing, founded by private ventures and governments. The other three technologies are still in early-stage conceptual design phase [6].

2 | Lead Cooled Fast Reactors

This chapter delves into the technological framework of Lead-Cooled Fast Reactors (LFRs). It begins by outlining the fundamental design principles and operational advantages derived from liquid lead coolants. Subsequently, the critical engineering hurdles hindering large-scale commercialization are examined, with a primary focus on the severe material degradation phenomena induced by heavy liquid metals and extreme radiation fields. To contextualize these technical challenges, the chapter concludes with an overview of the global research landscape. This progression ultimately highlights materials compatibility as the crucial bottleneck, establishing the necessary foundation for the subsequent analysis of corrosion mitigation strategies.

2.1. Design Principles of LFRs

Lead-Cooled Fast Reactors have become a global research hotspot as they promise to fulfill the advanced operational and safety criteria established for the next generation of nuclear power plants. However, their engineering implementation still faces key challenges that will be addressed in the following sections [15]. As a robust alternative to LWRs, lead-based systems address traditional vulnerabilities at their physical root. From now on, the focus will be on liquid lead, since for Gen IV designs LBE has been almost discarded due to high supply costs and production of radioactive Polonium-210.

The very high boiling point of liquid lead effectively precludes the potential for core uncovering due to coolant evaporation. Consequently, LFRs can be operated at near atmospheric pressure, eliminating the need for a heavily pressurized core vessel. Furthermore, such reactors could potentially be operated at temperatures up to 600 °C to enhance thermal efficiency. On the other hand, the high melting temperature of lead poses a serious freezing hazard and forces the introduction of robust auxiliary heating systems to prevent solidification during prolonged shutdowns [16].

Regarding neutronic behavior, lead has minimal moderating effect allowing LFRs to maintain a very hard neutron spectrum. This has severe implications on the reactor's operation

strategy: high energy neutrons maximize fuel consumption and the breeding ratio (BR). This parameter is defined as the ratio between the rate of fissile material produced over the rate of fissile material consumed. If this ratio is greater than 1, the reactor is called a "breeder" as it is able to produce more fissile material than consumed. This allows the reactor to operate with a completely self-sustained fuel cycle and, potentially, produce even excess fuel that can be exploited in other reactors. Thus, maximizing the BR of a nuclear reactor is mandatory to reduce the need of fresh mined uranium and avoid excessive reliance on external supply.

Regarding neutronic behavior, liquid lead exhibits a minimal moderating effect, allowing LFRs to maintain a highly energetic, "hard" neutron spectrum [17]. This has profound implications for the reactor's operational strategy: high-energy neutrons maximize both the efficiency of fuel consumption and the Breeding Ratio (BR) [14]. The BR is defined as the ratio of the rate of fissile material produced (transmuted from fertile isotopes) to the rate of fissile material consumed. If this ratio is greater than 1, the reactor operates as a "breeder", producing a net surplus of fissile material that can be extracted during reprocessing to fuel additional reactors. Consequently, maximizing the BR is a mandatory strategic objective for next-generation nuclear systems, as it virtually eliminates the reliance on freshly mined, enriched uranium and ensures long-term energy independence [18]. The typical fuel configuration employs highly enriched Plutonium-239, mixed with fertile Uranium-238, but LFRs are potentially compatible with Thorium cycle too [15].

Finally, liquid lead is a great coolant thanks to its large thermal conductivity and heat capacity. Moreover, its high thermal expansion coefficient provides a powerful driving force for natural circulation. This allows LFRs to heavily rely on passive decay heat removal systems, widening safety margins compared to Gen II reactors.

2.2. Technical Challenges and Barriers to Commercialization

While the inherent safety and sustainability of LFRs represent an attractive solution for future nuclear power production, the commercialization of such technology is contingent upon overcoming several unsolved engineering hurdles.

At elevated temperatures (exceeding 500 °C), liquid lead constitutes a highly aggressive environment where structural materials are subjected to phenomena such as dissolution-driven corrosion, oxidation, liquid metal embrittlement (LME), and erosion which can severely compromise the structural integrity of conventional nuclear grade steels [19].

This susceptibility represents a primary technological bottleneck in the deployment of LFRs; despite extensive research efforts over recent decades, the qualification of materials capable of withstanding long-term exposure remains a critical priority. These degradation mechanisms will be analyzed in detail in the following chapter, together with the possible mitigation strategies.

Furthermore, the hard neutron spectrum intensifies the radiation damage within structural components. Figure 2.1 illustrates the characteristic operational regimes of various nuclear reactor designs, mapping core temperature against radiation damage, which is quantified by the displacements per atom (dpa) metric. Dpa is a fundamental parameter representing the average number of times an atom is displaced from its equilibrium crystalline lattice site due to scattering collisions with energetic particles (predominantly fast neutrons in the case of an LFR core). As observed in the figure, the core of an LFR presents a substantially more hostile environment regarding radiation-induced material degradation when directly compared to conventional Generation II thermal fission reactors.

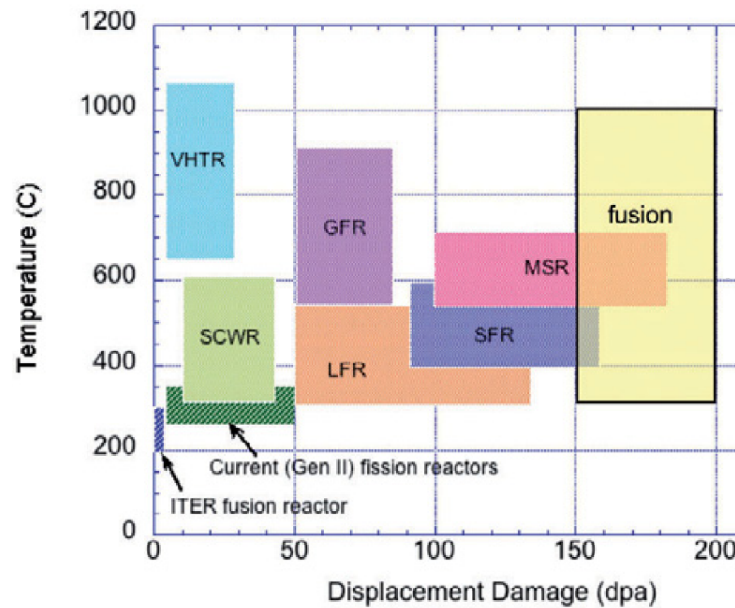


Figure 2.1: Overview of operating temperatures and displacement damage dose regimes for structural materials in current (generation II) and proposed future (Generation IV) fission and fusion energy systems. The six Gen IV fission systems are Very High Temperature Reactor (VHTR), Super Critical Water Reactor (SCWR), Lead Fast Reactor (LFR), Gas Fast Reactor (GFR), Sodium Fast Reactor (SFR), and Molten Salt Reactor (MSR) [20].

Another peculiarity of liquid lead, differentiating it from water, is its opacity. This makes in-vessel inspections and refueling particularly difficult, necessitating advanced ultrasonic

telemetry [6].

Finally, the extreme density of liquid lead makes LFRs' cores very heavy, this creates a big challenge: the need to effectively insulate the reactor from seismic events. State-of-the-art seismic technologies foresee the presence of high-damping supports below the whole nuclear island, but full scale tests are still needed [16].

Despite the engineering challenges outlined above, recent years have witnessed a major resurgence of interest in LFR systems from both public state corporations and private enterprises. The next section reviews the current status of the global research and deployment landscape.

2.3. Global Research Landscape

The idea of using LBE coolant for nuclear reactors is an old one: during the 1960s the Soviet Union built an entire fleet of submarines powered by this technology. Eight "Alpha-class" submarines were successfully operated until the 90s, highlighting both the great potential and the big concerns of such design. These reactors were developed under strict deadlines during the arms race and, full scale preliminary research was skipped: this led to early stage accidents. The first test reactor underwent core melting and other two further failures occurred, the main cause of the failures was attributed to a lack of knowledge of the LBE-steel interaction and to the poor control instrumentation installed. However, Russia accumulated 80 reactor-years of total operation and significant experience was obtained in the field of corrosion mitigation and maintenance operations [18, 21]. When the operation of these submarines officially concluded in 1996 [18], the research in lead-cooled technologies slowed down for a decade, until a renewed interest exploded with the nomination of LFR among the 6 concepts for Generation IV reactors [6].

In the past 20 years many designs were developed both in Western and Eastern countries and at present the deployment of LFRs is transitioning from scientific research to engineering qualification and demonstration phase. Russia remains the leader in the industry, relying on all the experience gained in the past. In Siberia the construction of the largest demonstration reactor, BREST-OD-300, is almost complete and the first criticality is planned for 2027 [22]. On the other side, in Europe, a multifaceted strategy is developing, with both public partners and heavy private investments. Key demonstrator projects include the ALFRED reactor in Romania and the SEALER commercial concept in Sweden. Furthermore, the MYRRHA accelerator-driven system (ADS) in Belgium is scheduled for commissioning in 2035. In the private sector, *newcleo* is actively developing its own designs in Italy, France and the US. Finally, also in China, Korea and Japan

studies are underway [6].

2.3.1. The Russian public project: BREST-OD-300

The BREST-OD-300 is the cutting-edge demonstration reactor developed by the Russian State Corporation Rosatom company. It aims at demonstrating the feasibility of closed fuel cycle with lead based technology, the power plant site hosts also all the facilities needed for fuel re-processing. Once in operation, it will represent a "first-of-a-kind" power plant, where all the fuel-handling activities will be carried out in the same location, nearby the reactor [23]. This reactor is the final product of a massive public effort, which started in 1998 with the first concept and took almost 30 years of work.

BREST-OD-300 features a pool-type integrated layout, in which the primary loop (core, steam generators, pumps and auxiliary systems) is housed inside a metal-concrete vessel, as depicted in Figure 2.2.

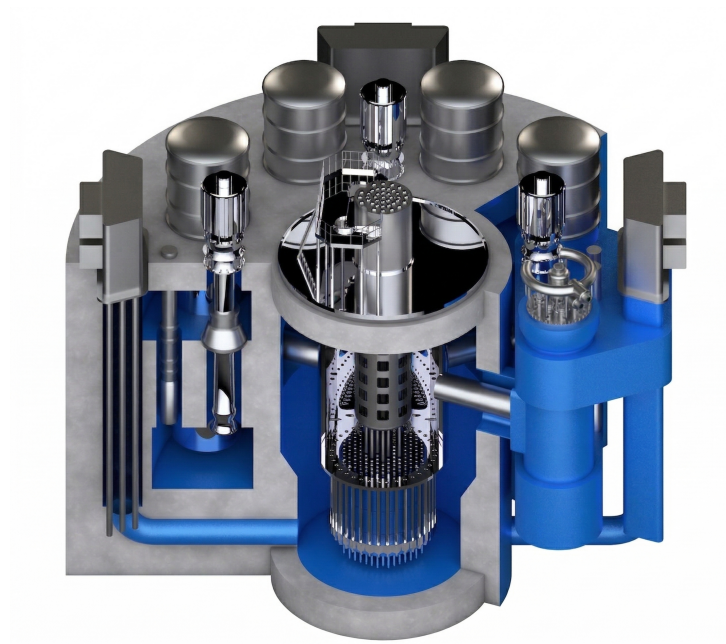


Figure 2.2: 3D render of BREST-OD-300 pool-type integrated layout. Courtesy of [24].

The primary coolant enters the core at 420 °C and exits at 537 °C, entering the steam generators where, in the secondary loop, superheated steam at 505 °C and 18 MPa is generated, achieving a surprising overall plant efficiency of 43% with the production of 300 MWe. In the future, temperatures are planned to be increased even further, to test the limits of materials [16].

The reactor uses innovative dense Mixed Nitride Uranium-Plutonium (MNUP) fuel, char-

acterized by high thermal conductivity and chemical stability, designed to improve thermal performance and mitigate proliferation risks [23]. Regarding structural steels, Russian engineers developed the EP-823Sh steel, a 12% Cr ferritic-martensitic steel with elevated silicon levels (1-1.3 wt.%). This steel was engineered explicitly for service in heavy liquid metals as it promotes the formation of a self-healing silica protective film, exploiting the oxygen dissolved in liquid metal [25, 23]. For the initial operational stage, the fuel cladding is designed to withstand a maximum burnup of 6%, while to achieve an economically viable burnup of 12% further improvements in materials are necessary. Oxide Dispersion-Strengthened (ODS) steels are the main candidates for future developments, although these materials still require qualification and licensing [19].

2.3.2. The European private venture: *newcleo*

In recent times numerous privately-funded start-ups have entered the nuclear market. They typically follow an opposite strategy with respect to public projects: reaching the final objective with a more aggressive approach, which typically means higher risks but also greater potential results. In Europe, *newcleo* has emerged as one of the strongest private ventures. Founded in 2021, they plan to build the first commercial Small Modular Reactors (SMRs), LFR-AS-30 (30 MWe, shown in Figure 2.3b) and LFR-AS-200 (200 MWe), within 2035 [26].

Simultaneously, *newcleo* is funding the construction of MOX (Mixed Oxide) fuel pilot production line in France, through which they plan to supply their future reactors and close the nuclear fuel cycle. In Figure 2.3a the concept of the reprocessing of spent fuel is depicted. *newcleo* has signed formal agreements with ENEA (Agenzia nazionale per le nuove tecnologie, l'energia e lo sviluppo economico sostenibile) to utilize the facilities of its Fusion and Nuclear Safety Department, located at the Brasimone Research Center, for extensive material testing and code verification. ENEA is a world leader in the liquid metal knowledge, with decades of research experience in the sector. The PRECURSOR facility is a 10 MWth pool-type integral testbed that perfectly mimics the layout of the LFR-AS-30 without using nuclear fuel. This system will be exploited to test core instrumentation and materials' behavior under corrosion. Regarding the structural materials, *newcleo* is implementing a wide experimental campaign to test both bare and coated steels, using materials which are already qualified for nuclear applications [17]. This, compared to the Russian approach, is a quicker and more direct way to solve the problems of liquid lead exposure: developing novel materials requires long and expensive technical studies and qualification procedures, which would not fit the stringent timelines of *newcleo*'s program.

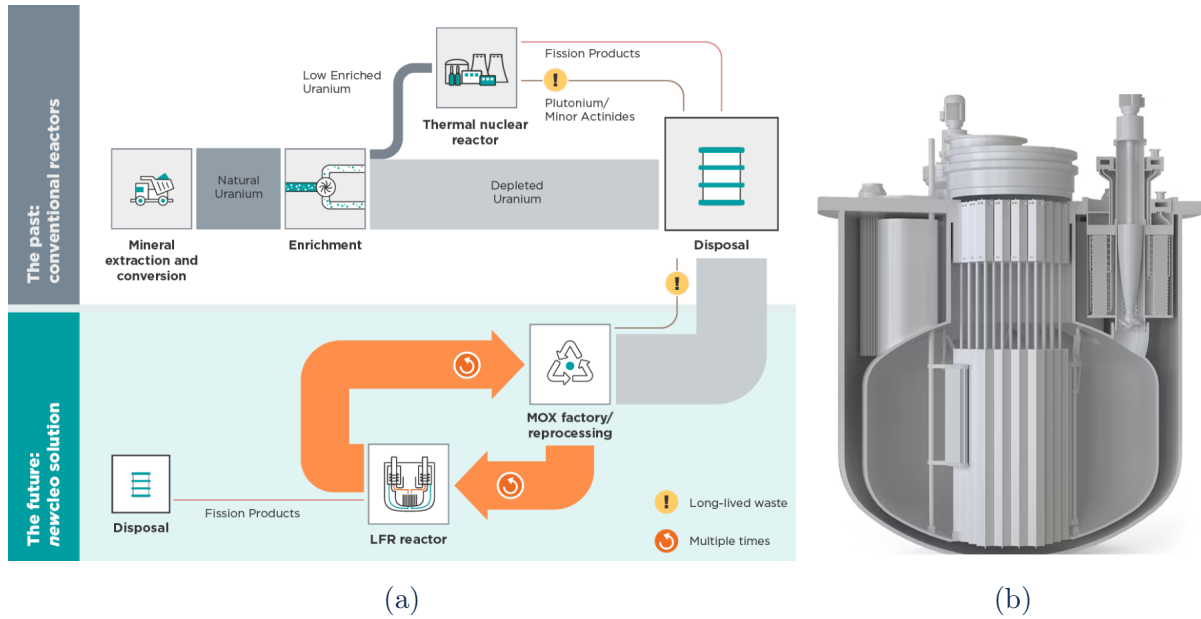


Figure 2.3: (a) Schematic of the closed fuel cycle: reprocessing of spent fuel to recover fissile materials, reducing waste volume, radiotoxicity, and reliance on uranium mining. Adapted from [26]. (b) Render of *newcleo*'s AS-30 demonstrator lead-cooled fast reactor design. Image courtesy *newcleo*.

To conclude, from the analysis of the development status of lead-cooled reactors, a great interest from the scientific community emerges and it is clear that this technology will play a crucial role in the energy mix of future generations. Nonetheless, key challenges remain; specifically, the problem of materials compatibility represents the primary bottleneck for industrial deployment. Consequently, the development of robust mitigation strategies is an essential prerequisite for the successful commercialization of LFRs. Situated within this broader research framework, the present work focuses on the investigation and evaluation of potential candidate materials for protective systems. However, to effectively address this challenge, a rigorous understanding of the underlying degradation mechanisms in heavy liquid metal is mandatory. Therefore, the next chapter provides a comprehensive review of these corrosion phenomena.

3 | Liquid Metal Corrosion in Lead-Cooled Reactors

This chapter provides an overview of the environmental degradation phenomena affecting structural materials exposed to the high temperature liquid lead. The interaction between steel and liquid lead is governed by a complex interplay of competing degradation mechanisms, namely oxidation, dissolution corrosion, erosion, and liquid metal embrittlement. To provide a structured framework, this chapter first outlines the principal candidate alloys, details the physical drivers of each degradation phenomenon, and subsequently evaluates the most viable mitigation strategies. This progression ultimately establishes the technological rationale for selecting advanced chromium coatings, which constitute the core experimental focus of this thesis.

3.1. Candidate Structural Materials

The environmental degradation induced by liquid lead originates from the inherent incompatibility between the candidate structural materials and the liquid lead environment [27]. To comprehensively evaluate these degradation mechanisms it is essential to define the microstructural properties and the composition of the alloys considered for LFR applications. Near-term candidates include Austenitic Stainless Steels (AuSS) and Ferritic/Martensitic (F/M) steels. Table 3.1 reports the compositions of the main structural steels currently under consideration for this role. Other solutions like ODS steels, the MAX phases, SiC fiber-reinforced SiC and refractory metals are under investigation for longer-term material perspective [28].

F/M steels have the body-centered cubic structure and exhibit a good combination of mechanical properties up to 600 °C, high thermal conductivity, low thermal expansion and superior resistance to void swelling (up to 160 dpa) and to helium embrittlement. For nuclear applications the optimal Cr wt.% is 9, which minimizes the ductile-to-brittle transition temperature. T91 (9Cr-1Mo) is arguably the most studied material of the family and it is already qualified for pressure vessels in thermal reactors [20, 27].

Table 3.1: Chemical composition (wt.%) of the main candidate structural steels for LFR applications. Adapted from [28].

Steel Grade	Cr	Ni	Mo	Mn	Si	C	Ti	Others
<i>Ferritic-Martensitic Steels</i>								
T91	8.0-9.5	0.11	0.89	0.38	0.22	0.10	-	V, Nb, N
EP-823	10.0-12.0	≤ 0.1	0.6-0.9	0.4-0.6	1.1-1.3	0.14-0.18	-	V, Nb, W
<i>Austenitic Stainless Steels</i>								
316L	17.0	10.0-14.0	2.0	1.8	0.6	0.03	-	N, P, S
316Ti	16.0	14.0	2.5	1.7	0.6	0.05	0.4	-
15-15Ti (1.4970)	15	15	1.2	1.5	0.4	0.1	0.5	B

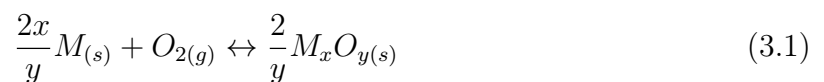
Among Austenitic Stainless Steels (with face-centered cubic structure), 316L AuSS has been extensively used as fuel cladding in SFRs, showing good radiation resistance and low creep at temperatures below 475 °C. Ti-stabilized AuSS, like the 316Ti grade and the 15-15Ti class, contain precipitates of titanium where radiation-induced defects can recombine, reducing void swelling. In addition, increasing Ni to Cr ratio reduces the mobility of vacancies and so improves radiation resistance even further. Additionally, AuSS do not exhibit ductile-brittle transition [28].

3.2. Oxidation

Oxygen is inherently dissolved in the liquid lead used in LFRs, causing the oxidation of the wetted surfaces. When the formed oxide films are thin, compact and defect-free, resistant to spontaneous spallation and possess low Pb/O diffusion coefficients at reactor-relevant temperatures, they can play a crucial role in protecting steel substrate from Liquid Metal Corrosion (LMC) attack. On the other hand, if oxide layers grow in thickness, the heat transfer capability of components is worsened and the probability of failure due to thermal stresses accumulation increases [29]. If well exploited, formation of self-healing protective oxide scales over structural materials is fundamental to inhibit degradation.

3.2.1. Thermodynamics of Steel Oxidation

The oxygen concentration dissolved in Pb (C_0) is a critical parameter affecting the corrosion behavior of steels in LM. Metals react with the dissolved oxygen according to Equation 3.1.



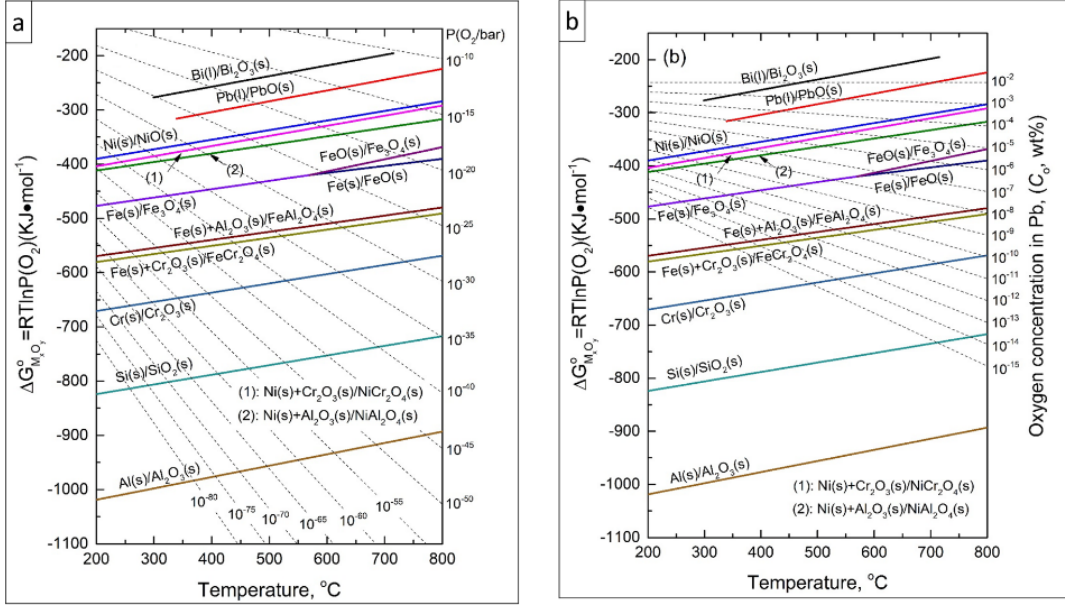


Figure 3.1: Ellingham diagrams of the standard Gibbs free energy of oxide formation per mol O₂ (left y-axis) as a function of: (a) the oxygen partial pressure in the gas plenum above the HLM melt, (b) the concentration of dissolved oxygen in liquid Pb and liquid LBE, respectively, (right y-axis), and temperature (x-axis) for the formation of oxides due to the oxidation of the main steel alloying elements in liquid Pb. [30]

In Figure 3.1 Ellingham diagrams of the standard Gibbs free energy of oxide formation are reported. The lower the equilibrium line, the easier the formation of the corresponding oxide. By looking at Figure 3.1, Cr, Si and Al are good elements to prevent iron oxidation, since their Gibbs free energy of oxide formation is lower than the one of magnetite (Fe_3O_4), even for low oxygen content. Preventing the growth of magnetite is a strict requirement for structural integrity, as it is a highly porous and non-protective oxide that cannot shield the underlying steel from liquid lead attack. Therefore, protection relies on the stable oxides of Cr, Si, or Al. Such oxide scales can come either from *in situ* formation (as a result of the exposure of alloyed steels to oxygen-containing liquid Pb) or when applied in the form of coatings on the steel surface [28].

Figure 3.1 reports the Ellingham diagram for the standard Gibbs free energy of oxide formation. The lower the equilibrium line, the more thermodynamically favored the formation of the corresponding oxide. Consequently, Cr, Si, and Al act as excellent protective elements against iron oxidation. Since their Gibbs free energies of oxide formation are significantly lower than that of magnetite (Fe_3O_4), they preferentially oxidize even at very low oxygen contents. Such protective scales can be achieved either via *in situ* formation (when alloyed steels are exposed to oxygen-containing liquid Pb) or when applied

as engineered surface coatings [28].

Figure 3.2 presents a simplified visualization of how C_0 affects the relative occurrence of dissolution (named "liquid metal corrosion") and oxidation, in two tested AuSS. At C_0 between 10^{-7} and 10^{-6} , both phenomena are expected, but the corrosion depth is minimized, highlighting the effectiveness of in situ formation of protective oxide scale for C_0 in this range [31].

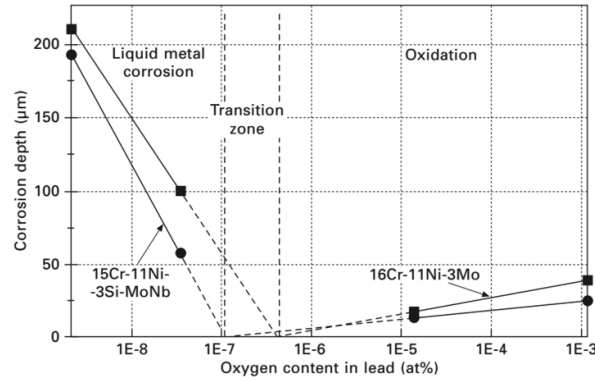


Figure 3.2: Effect of the dissolved oxygen concentration on the behavior of two different AuSS exposed to liquid Pb for 3000 h at 550 °C. [31, 32]

For low C_0 steels cannot form protective oxide scales and dissolution of alloying elements is free to advance. On the other side, for high oxygen content another problem arises: above the solubility limit of oxygen in liquid Pb, oxidation of the coolant itself occurs, leading to the precipitation of solid lead (PbO) crystals. This precipitation creates solid slag that can be source of severe damage to core components and plug narrow channels [19].

3.2.2. Kinetics of Steel Oxidation

In principle, since oxidation is a diffusion-dominated process, the formation of an oxide scale should follow a parabolic growth (according to Wagner theory) [28]. However, wide experimental campaigns conducted on steel corrosion in liquid metal environment highlight a more complicated behaviour. The specifics of the formed oxides strictly depend on the considered steel. As an example, the typical oxidation characteristics of F/M steels are presented. As visible in Figure 3.3a, F/M steels form a duplex oxide scale: the outer region is composed of generally porous and less protective scale composed of magnetite (Fe_3O_4) whereas the inner part is made of a denser and more protective scale composed of FeCr-spinel oxide ($Fe(Fe, Cr)_2O_4$) [33]. Figure 3.3b shows a schematic representation of the model developed by Martinelli et al. [34] for T91 based on "available space model".

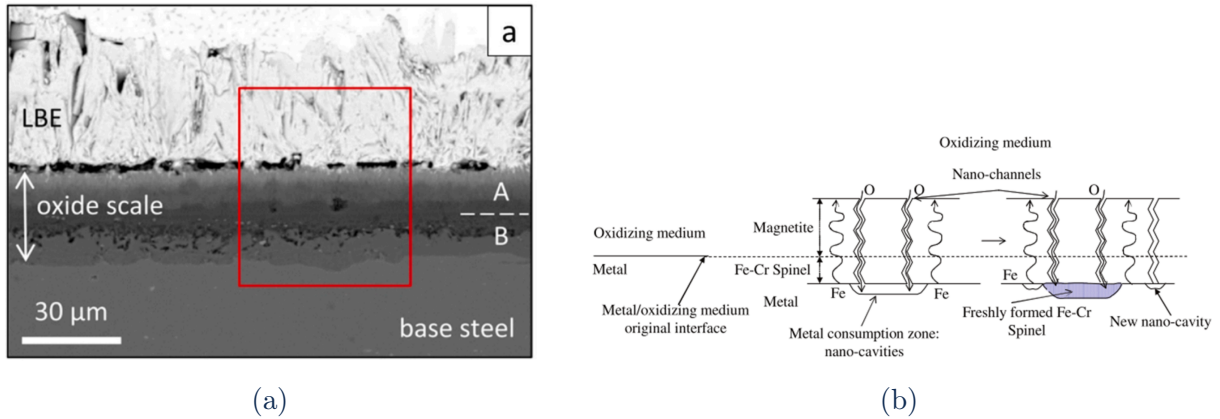


Figure 3.3: **(a)** SEM images of the complex oxide scale on Si-doped EP-823 F/M steel exposed to oxygen-rich, static LBE at 490 °C for 5016 h. The oxide film consists of magnetite (area A), FeCr-spinel (area B). Adapted from [33]. **(b)** Schematic representation of the oxidation mechanism of F/M mechanism based on the "available space model" [34].

This model considers a parabolic growth of the outer magnetite scale (thanks to the outward diffusion of Fe cations). The FeCr spinel grows inward at the oxide/steel interface in the nano-cavities generated by the coalescence of vacancies left behind by Fe migration. Above these cavities Pb nano-channels form through a dissociative or perforative growth process. O diffuses through the HLM channel, reacts with steel to form Fe-Cr spinel until the cavity is filled. This process, iterated in time, leads to the structure observed in Figure 3.3a [34].

3.3. Dissolution Corrosion

Besides oxidation, dissolution corrosion is an important LMC mechanism that originates from the high and temperature-dependent solubility of steel alloying elements in HLMs. This process is facilitated by intimate contact between the steel and the HLM (when a protective oxide scale is missing) but can also occur by elemental diffusion through an oxide layer. This material degradation can either be relatively uniform or locally enhanced. Dissolution pits are regions where the dissolution-affected depth is much larger than the surrounding area and often nucleate at pre-existing steel defects [28].

Since each element has different solubility in Pb, selective leaching is likely to take place. The elemental dissolution of austenite stabilizers (Ni and Mn) results in the ferritization of the dissolution-affected areas in AuSS. Furthermore, mass transfer phenomena can occur in non-isothermal cores: due to the temperature dependence of the solubility limit, dissolved species from hotter regions can precipitate in colder ones; this is particularly

true for Fe, given its low solubility limit at low temperature (visible in Figure 3.4) [35].

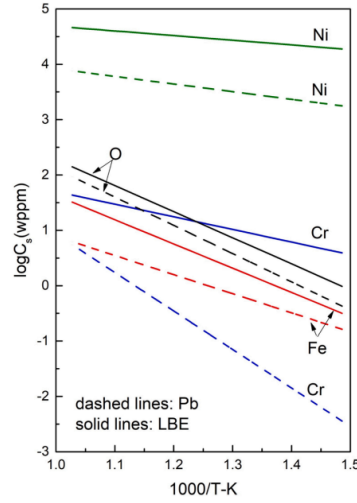


Figure 3.4: Solubility of Fe, Cr, Ni, and O in liquid Pb and liquid LBE as a function of temperature, adapted from [28].

The dissolution corrosion mechanism can significantly alter the chemical composition of the steel up to depths of several hundred micrometers. As alloying elements selectively leach into the coolant, a network of nano-cavities is generated; these voids are subsequently infiltrated by oxygen-depleted liquid metal. This process establishes a preferential percolation path for the inward migration of the liquid metal, thereby accelerating dissolution of the bulk material. On the microscopic level, selective leaching proceeds one grain at a time, starting from intergranular penetration of HLM. For this reason, in many studies, finer-grained steels were found more susceptible to both uniform dissolution and pitting attacks [36].

Finally, also the HLM flow pattern plays a crucial role in dissolution corrosion. For low coolant velocities, the overall leaching rate is governed by the slow mass transfer of dissolved steel alloying elements across the fluid boundary layer adjacent to the steel surface. For high flow rates, instead, the mass transfer in the boundary layer becomes so fast that the dissolution rate becomes controlled by the actual dissolution reactions occurring directly at the HLM/steel interface. Furthermore, local instabilities in the flow pattern are identified as major cause of dissolution pits. Conversely, flow patterns that create poorly flushed areas are equally problematic: these regions can lack oxygen replenishment, inhibiting the formation of protective oxide scales [28].

3.4. Erosion/Corrosion Mechanism and Fretting Wear

Erosion may be considered as the mechanical ablation of steel components exposed to a fast-flowing HLM, it is often observed when liquid metal transports solid particles (oxides, carbides) and where HLM flow has local disturbances (e.g. eddies). This effect can combine with dissolution attack, which tends to create loose grains via the intergranular HLM penetration. The result is the detachment of big grain clusters which imparts a jagged appearance to the steel's surface. The process is schematized in Figure 3.5.

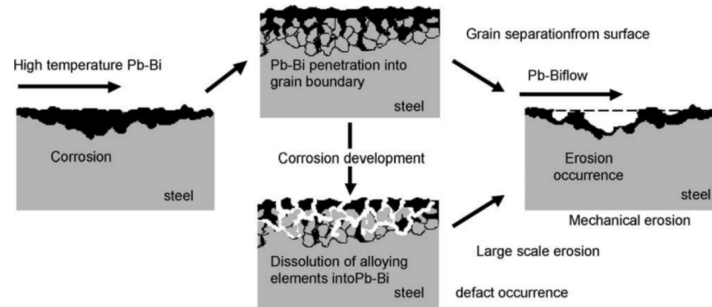


Figure 3.5: Schematic illustration of an erosion/corrosion mechanism [37]

Another failure mechanism resulting from the combination of corrosion and mechanical loads is fretting wear. This process often takes place at the contact between fuel cladding tubes and spacer grids: here vibrations triggered by HLM flow can dangerously enhance corrosion. This problem has been identified as the primary failure mechanism of fuel assemblies of commercial Gen-II/III reactors and is expected to affect the performance of LFR fuel assemblies as well [28].

3.5. Liquid Metal Embrittlement

Liquid Metal Embrittlement (LME) is a degradation process occurring in load-bearing materials when wet by liquid lead, which causes reduction in ductility, toughness, fatigue life and creep resistance. This process occurs at atomic scale but is influenced by several mesoscale effects of the HLM/steel superficial interaction (e.g. LMC) and by the stress state of the components. Other phenomena that alter materials' mechanical properties, such as radiation damage and high temperature exposure play a key role in the effects of the embrittlement process [38].

In the scientific community no single unified theory is available, and engineers typically

have to rely on several atomic-scale models to explain LME. What is clear is that three fundamental prerequisites must be simultaneously satisfied for LME to take place: wetting of the surface by HLM, presence of a threshold tensile stress in the material and localized plastic deformation. However, all cited models agree that it is the adsorption of Pb atoms that reduces cohesion between steel atoms and facilitates crack propagation in steels. The final effect of LME is the catastrophic transitioning of normally ductile steels into a highly brittle state, where failure can occur at any moment with minimal elongation [28]. The LME susceptibility of a component depends on a wide range of factors that can be classified in three categories: intrinsic steel sensitivity (wettability), steel alteration due to irradiation and kinetic factors (temperature, applied strain, HLM oxygen concentration) [39]. AuSS steels are almost immune to the embrittlement process, thanks to their FCC structure. Regarding the temperature dependence, it has been observed that LME is dangerous at intermediate temperature, while it vanishes for temperatures outside a critical window (characteristic of each HLM/steel couple) [28].

3.6. Mitigation Strategies

As already discussed, issues related to materials compatibility inside LFRs cores are arguably the biggest obstacle to the commercialization. The first solution that may be considered is the optimization of the reactor system design, which must point in the direction of minimizing the materials degradation. The temperature dependence of most of the processes discussed in previous sections highlights the key role of temperature. It is often considered to lower the nominal operation temperature range of the reactor, to prevent heavy degradation of materials. However, this goes against the economics of nuclear plants, in terms of thermodynamic efficiency and possibility of exploring new markets (heat production, hydrogen production), both of which become economically convenient for operating temperatures in the higher range (above 500°C). Moreover, the optimization of reactor design must avoid local flow instabilities that enhance localized erosion/corrosion. Other than these precautions, there are several candidate measures to mitigate undesired LMC effects such as active oxygen control, development of innovative materials and advanced protective coatings [28].

3.6.1. Active Oxygen Control

Active Oxygen Control (AOC) is a primary mitigation strategy. The need for a precise AOC system emerged since the operation of the first Soviet submarines in the 1960s. The core concept is to maintain the oxygen concentration in the core within a precise thermo-

dynamic range, in order to promote the formation of protective oxide scales on structural materials, while preventing the dangerous precipitation of solid PbO agglomerates. Many technological solutions have been developed but key problems still need to be solved in modern LFRs designs [19].

AOC can be achieved by injecting either hydrogenated or oxygenated gases into liquid lead, in order to actively take oxygen out of the solution or increase the oxygen content. This solution has been pioneered in Soviet nuclear submarines, proving great efficiency and long-term robustness [40]. Alternatively, solid-phase mass exchangers and electrochemical oxygen pumping are under testing phase. Despite the modern advancements in AOC systems, the reliability of such techniques for commercial LFRs is intrinsically limited due to the strong temperature dependence of oxygen solubility in liquid lead, which poses severe risks of PbO precipitations in the colder parts of the core. Secondly, it is very easy in large reactor pools to develop stagnant regions where the localized oxygen concentration can decrease a lot, inhibiting the formation of protective oxide scales. Due to these concerns, the modern reactor programs are evolving their strategy towards "passive" mitigation strategies, which ensures an intrinsic robustness of structural materials against LMC [19].

3.6.2. Advanced Structural Materials

The addition of strong oxide-forming elements (Cr, Al, Si) to either the bulk or the surface of structural materials has been demonstrated to be an effective LMC mitigation method. In particular, Alumina Forming Austenitic (AFA) steels have shown good resistance. On the other hand, adding Al to F/M steels caused a degradation of LME resistance, due to Al-induced solid solution strengthening, which in F/M steels exacerbates the intrinsic brittleness of the bcc structure [28]. Al-enriched High Entropy Alloys proved to form protective Cr_2O_3 and Al_2O_3 and are considered good candidates for long term deployment. Even though doping the bulk steel with Si and Al improved LMC resistance, mechanical properties were reported to deteriorate [41]; this issue could be overcome by enriching with such elements only a superficial steel layer. In this way it is possible to protect the material while leaving the bulk properties unaltered. Another relevant surface treatment is nanocrystallization, which demonstrated to improve the oxide scale formation kinetics by offering more paths for the outward diffusion of Al and Cr [28]. Engineering of superficial grain boundaries can be beneficial too. Murty and Charit [42] pointed out that through suitable annealing and thermomechanical processes it is possible to produce certain coincident site lattice grain boundaries (GBs), improving resistance to intergranular corrosion, thermal creep and LBE penetration [42].

3.6.3. Coatings

The deposition of thin protective coatings is arguably the most viable short term solution to solve materials compatibility issues in LFRs. This approach allows for the use of already qualified steels, avoiding the development of brand-new structural materials and dramatically reducing the time required for testing and qualification [28].

Among the candidate materials for such coatings, refractory metals (W, Mo, Ta) and their alloys exhibit very low solubility in liquid Pb and can effectively shield the substrate from dissolution attacks. However, they are very susceptible to oxidation, forming unstable scales, and are highly vulnerable to radiation-induced embrittlement at reactor relevant temperatures. Despite their great anticorrosive potential, these drawbacks hinder their widespread application in reactor cores [28].

MAX phases are a family of ternary carbides or nitrides defined by the general formula $M_{n+1}AX_n$ where M is an early transition metal, A is an element from group 13-16 and X is carbon or nitrogen. These materials show excellent compatibility with HLM, but their low fracture toughness poses serious questions about their use in LFRs [28].

Two very promising ceramic candidates are Alumina (Al_2O_3) and ZrO_2 . Alumina coatings demonstrated the potential to overcome the brittleness of other ceramics [43]. Recently, nanocrystalline/amorphous alumina coatings deposited with Pulsed Laser Deposition (PLD) have been tested in stagnant liquid Pb with $C_O \approx 10^{-8}$ for 4000 h. The results from Ferrè et al. [44] proved that Al_2O_3 can prevent LMC attack to the 15-15Ti AuSS substrate, even in corrosion + irradiation tests. In Figure 3.6 the uncoated steel shows clear signs of LMC and Pb penetration, whereas the coated sample exhibits no trace of failure, even at microscopic level. A primary concern with alumina coatings is their lack of self-healing capability. If a micro-crack breaches the protective film, spontaneous regeneration is impossible as there is no free aluminum available to react with the oxygen dissolved in the liquid lead.

A valid alternative to inert coatings, like the one described above, is Al, Si and Cr containing metallic coatings, which develop dense and protective oxide scales when exposed to oxygen-containing liquid lead. Many compounds are under investigation, among which FeCrAlY and FeCrAlNi mixes showed great performances. These coatings can be produced via Physical Vapour Deposition techniques like Magnetron Sputtering in combination with GESA (Gepulste ElektronStrahl Anlage), a technique used to improve coatings adhesion and reduce their porosity [45]. The complex crystalline matrix of these coatings and the ability to develop self-healing alumina scales can efficiently block diffusion processes. The presence of chromium has demonstrated to play a key role in the effectiveness

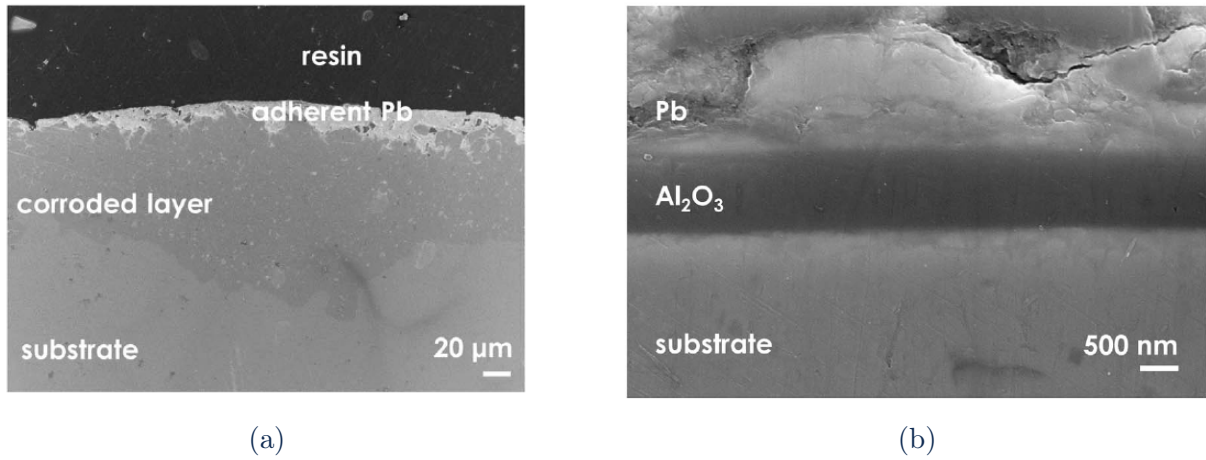


Figure 3.6: SEM images of uncoated 15-15Ti cylinder (a) and coated one (b) after the corrosion test in stagnant lead at 550°C for 4000 hours with $C_O \approx 10^{-8}$ wt.%. Adapted from [44].

of the coatings [28].

Chromium itself, in fact, represents a great option for coatings. Its anticorrosive properties are widely known, and it has been employed in the conventional industry for decades for protecting surfaces both as coating and as alloy element in steels [28]. Many studies have emerged recently about the application of chromium coatings in the nuclear industry, for the production of advanced Accident Tolerant Fuels (ATFs) for LWRs and for mitigation of LMC in lead-cooled reactors [46, 47]. Chromium shows potential for resolution of many issues associated with the other possibilities, like the inherent brittleness and total lack of self-healing capabilities of monolithic ceramics, the heavy Liquid Metal Embrittlement (LME) susceptibility due to Aluminum additions in FeCrAl-type metallic coatings, and the relatively low fracture toughness of MAX phases. In light of these advantages, this thesis will focus on chromium coatings, which will be described in detail in the following chapter.

4 | Anticorrosive Chromium Coatings

Building upon the critical need for effective corrosion mitigation strategies established in the previous chapter, this chapter introduces metallic chromium as a candidate material for protective coatings in heavy liquid metal environments. It begins by detailing the fundamental physico-chemical, optical, and structural properties of chromium and its highly stable oxide, chromia (Cr_2O_3). Subsequently, a comprehensive review of state-of-the-art manufacturing techniques, with a focus on High Power Impulse Magnetron Sputtering (HiPIMS), and current nuclear applications is presented. This review highlights a distinct lack of experimental data concerning the oxidation kinetics and liquid lead compatibility of HiPIMS-deposited chromium films. Finally, the chapter concludes by defining the research objectives and outlining the experimental strategy adopted.

4.1. Chromium and its Anticorrosive Capability

Chromium is a first-row transition metal with $Z = 24$ and, in pure form, exhibits BCC crystalline structure.

Table 4.1: Physico-chemical and thermo-mechanical properties of pure Chromium.

Property	Value
Atomic Number (Z)	24
Density	7.19 g/cm^3
Melting Point	$1907 \text{ }^\circ\text{C}$
Thermal Conductivity	$\approx 93.9 \text{ W/(m}\cdot\text{K)}$
Coefficient of Thermal Expansion (α_{Cr})	$\approx 9.5 \times 10^{-6} \text{ K}^{-1}$
Electronic Structure	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
Electronegativity (Pauling scale)	1.66
Thermal Neutron Absorption Cross-Section	3.1 barns

In Table 4.1, the key properties relevant for this work are summarized. Chromium's

high melting point, superior thermal conductivity, and neutron transparency make it an ideal candidate for nuclear environments. Moreover, what makes this element particularly appealing for anticorrosive coatings is its affinity with oxygen: when a Cr layer is exposed to an oxygen-containing atmosphere, oxide scale grows very easily. The properties of the formed oxide strictly depend on the thermodynamic conditions, among which oxygen partial pressure and temperature are dominant [48, 49].

4.1.1. Chromium (III) oxide

Given its electronic structure, chromium exhibits oxidation states in the range -4 to +6, which allows it to form several oxide compounds [50]. Examples of such oxides are CrO, CrO₂, CrO₃, Cr₃O and Cr₂O₃ [51]. According to Khojier et al. [52], who investigated the properties of chromium oxide scales prepared by post annealing of Cr thin films, Cr₂O₃ is the only stable oxide at reactor-relevant thermodynamic conditions (above 500°C).

Cr₂O₃ (also known as chromium(III) oxide or chromia) has the corundum structure shown in Figure 4.1, belonging to $R\bar{3}c$ space group and consisting of a hexagonal close packed array of oxide anions with two thirds of the octahedral holes occupied by chromium atoms [50, 52].

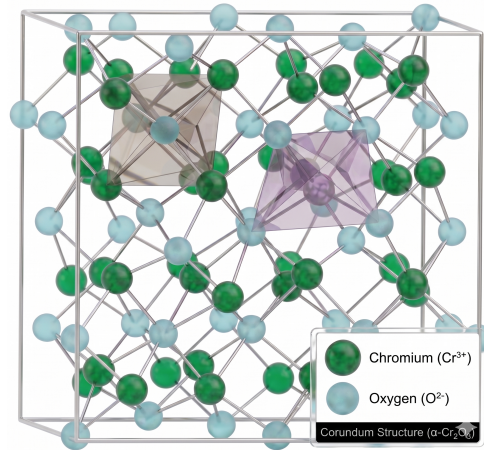


Figure 4.1: Schematic representation of corundum structure of Cr₂O₃, showing octahedral coordination of Cr³⁺ ions and tetrahedral of O²⁻. Adapted from [53]

This densely packed lattice severely restricts the mobility of atoms through it, acting as an efficient kinetic barrier [54]. For instance, at 600 °C, the diffusion coefficient of oxygen in Cr₂O₃ is incredibly low ($9.24 \times 10^{-29} \text{ m}^2 \text{ s}^{-1}$), and that of iron is similarly restricted ($1.53 \times 10^{-22} \text{ m}^2 \text{ s}^{-1}$) [54]. Additionally, as visible in Figure 3.1, the Gibbs free energy of oxide formation is largely negative (below -600 kJ/mol) at 600°C, indicating that the formation of chromia is spontaneous and thermodynamically favored even at

high temperatures [55] and low oxygen partial pressures (well below the partial pressures expected in LFRs, where the oxygen content will be 10^{-7} wt%). Moreover, chromia, unlike alumina, is stable up to 1000°C even in the harshest environments [56].

Chromium(III) oxide has another optimal characteristic: its Pilling-Bedworth Ratio (PBR) is 2.07. PBR is defined as the ratio of the volume of the metal oxide produced to the volume of the corresponding metal consumed during the oxidation reaction. This means that when Cr_2O_3 grows above pure Cr, it covers the whole surface without discontinuities and it intrinsically develops a compressive stress state, which is beneficial for the mechanical stability of the oxide scale [47].

4.1.2. Raman Spectra of Chromium (III) Oxide

Since Raman spectroscopy is the standard non-destructive technique used for the structural characterization of oxides, and was extensively used in this experimental thesis project, this section details the characteristics of Raman signal of Cr_2O_3 . Further technical details regarding the Raman spectroscopy methodology are provided in Section 6.2.

From theoretical calculations based on Group Theory, the irreducible representation for the optical mode of chromia in rhombohedral corundum structure is:

$$\Gamma_{\text{opt}} = 2A_{1g} + 2A_{1u} + 3A_{2g} + 5E_g \quad (4.1)$$

Here, only $2A_{1g}$ and $5E_g$ are Raman active modes [57].

Hosterman et al. [58] recorded the Raman spectra of a bulk, stress free, Cr_2O_3 single crystal at room temperature and found 6 of the seven predicted modes. The results are shown in Figure 4.2.

The most intense peak at 552 cm^{-1} is assigned to a symmetric vibration (A_{1g}) of crystal associated with the stretching of the strong Cr-O bonds in the fundamental octahedra CrO_6 [59]. Conversely, the E_g modes are associated to asymmetric stretching vibrations or bending modes [57, 60, 61]. Monnerau et al. [62] highlights that the peak at 398 cm^{-1} is not universally associated to Raman scattering. This weak line in the spectrum is, in some papers, attributed to a one-magnon scattering of the impinging light. Through a combination of DFT calculations and high energy resolution vibrational electron energy-loss spectroscopy (EELS), Idrobo et al. [63] demonstrated that the low-frequency vibrational modes of Cr_2O_3 are primarily associated with chromium dynamics, whereas the high-frequency optical branches (above 70 meV) are dominated by oxygen motion (see Figure

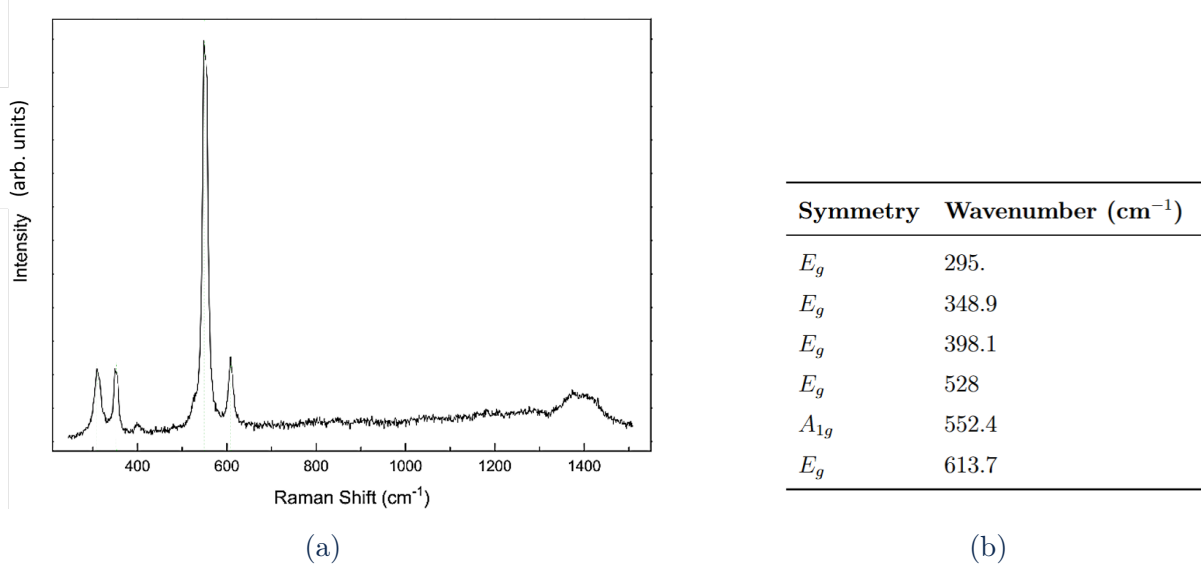


Figure 4.2: (a) Reference Raman spectrum of stress free, bulk monocrystal of Cr_2O_3 measured by Hosterman et al. [58] with a 514 nm laser source; alongside the corresponding assignment of Raman-active modes (b).

4.3). This result perfectly aligns with the classical "mass on a spring" model, which predicts that the frequency of a vibrational mode is proportional to $1/\sqrt{m}$, where m is the mass of the atoms involved.

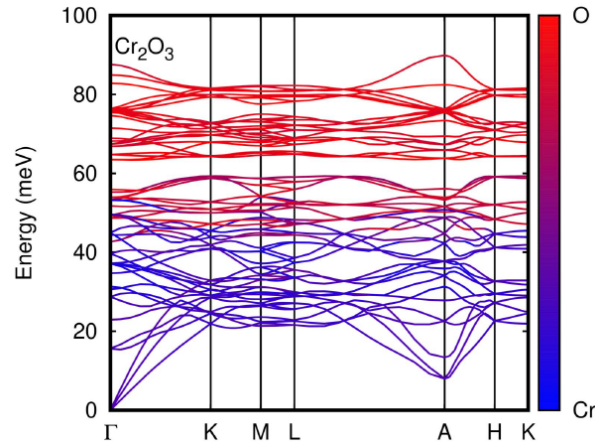


Figure 4.3: Calculated phonon dispersion for Cr_2O_3 . [63]. The color scale represents the relative atomic contributions, from Cr-dominated modes (blue) to O-dominated phonon modes (red). Optical branches above 70 meV are primarily oxygen-derived.

Furthermore, Raman spectroscopy is a useful tool to evaluate the stress state of a material, as the position of Raman peaks is highly sensitive to the presence of stresses within the crystalline lattice. In particular, regarding how residual stresses modify the Raman

spectrum of Cr_2O_3 , Kemdehoundja et al. [64] exploited in situ Raman spectroscopy to monitor the stresses developed during high-temperature oxidation process of NiCr30 alloy (which forms pure Cr_2O_3 under high temperature oxidation). According to this work the shift of the wavenumber of the principal peak A_{1g} at 552 cm^{-1} can be related to the stress in the oxide using the following relation:

$$\sigma[\text{GPa}] = \Delta\nu[\text{cm}^{-1}] \cdot 0.307 \pm 0.005 \quad (4.2)$$

Where $\Delta\nu = \nu_c - \nu_L$. Consequently, a positive $\Delta\nu$ indicates a state of compressive stress ($\sigma < 0$), whereas a negative shift corresponds to tensile stress ($\sigma > 0$). This same correlation was confirmed by Mougin et al. [60] and by Birnie et al. [65].

Mohammadtaheri et al. [66] analyzed the evolution of the Raman spectra of Zr-doped Cr_2O_3 coatings (synthesized via magnetron sputtering) upon crystallization. . In the as-deposited amorphous state, the lack of long-range translational symmetry leads to a total relaxation of the momentum conservation rule. Consequently, the Raman spectrum is no longer restricted to phonons at the Brillouin zone center ($q \approx 0$) and instead becomes a projection of the entire phonon density of states (further details about selection rules for Raman scattering are discussed in Section 6.2.1). This results in the broad, featureless bands observed in the as-deposited spectrum (Figure 4.4, black line). Upon annealing, the restoration of long-range lattice periodicity re-imposes the Raman selection rules, resulting in the appearance of the sharp, well-defined vibrational modes shown in Figure 4.4 (red line), representative of a fully crystalline film.

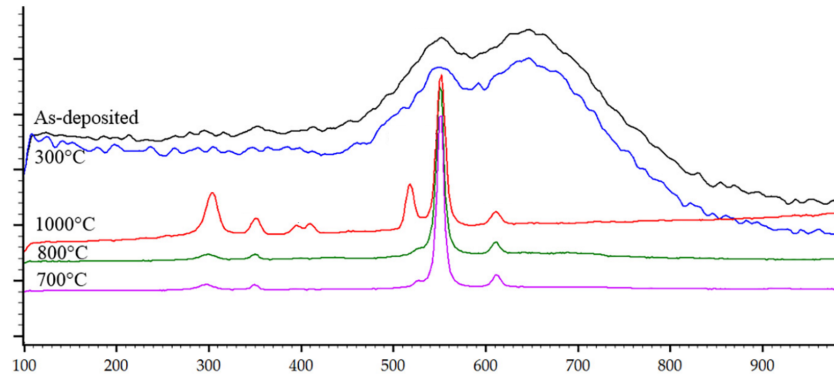


Figure 4.4: Raman spectra of Zr-doped chromia coatings after heat treatment at the indicated temperature. Adapted from [66].

4.1.3. Optical Properties of Chromium (III) Oxide

In this section the electronic structure characterizing thermally grown Cr_2O_3 is described in order to provide a theoretical background for the analysis developed in Chapter 8.

First-principles density functional theory (DFT) and experimental optical measurements demonstrate that chromia has a direct optical band gap of around 3.3 eV [67, 53]. Khalaf et al. [68] observed that in annealed chromia films this value can reduce to 3 eV due to variation in the grain size and crystalline defects generating tail states near the valence and conduction bands.

In corundum structure of Cr_2O_3 , Cr^{3+} ions are positioned in the distorted octahedral electrostatic field formed by the surrounding oxygen anions, and the three remaining valence electrons occupy 3d orbitals. In such configuration the spherical symmetry of d orbitals and their degeneracy is removed. The five d orbitals are thus split into two distinct energy levels: a lower-energy triplet state t_{2g} and a higher-energy doublet state e_g [50]. The three valence electrons naturally populate the t_{2g} orbitals with parallel spins. The valence band of chromia crystal is dominated by oxygen 2p orbitals whereas valence band is formed mostly of empty chromium e_g orbitals. As a result the observed direct band gap of 3 eV is associated to charge-transfer transitions from oxygen 2p to chromium 3d orbitals [69].

However, if the absorption spectrum of Cr_2O_3 is observed, a strange behavior can be detected. As reported by Bhardwaj et al. [57], while the fundamental band-to-band transition is located in the ultraviolet region at 368 nm, the visible range of the spectrum exhibits distinct absorption features driven by localized intra-band d-d electronic transitions of the Cr^{3+} ions. Specifically, the authors highlight two prominent, spin-allowed absorption peaks: a peak at 460 nm, which is assigned to the electronic transition denoted as ${}^4A_{2g} \rightarrow {}^4T_{1g}$; and a peak at 610 nm, which corresponds to the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition. Furthermore, two additional weaker features are identified, described as "frail shoulders", located at 680 nm and 715 nm. They attribute these specific features to spin-forbidden intra-band transitions, identifying them as the ${}^4A_{2g} \rightarrow {}^2T_{1g}$ and ${}^4A_{2g} \rightarrow {}^2E_g$ transitions, respectively.

The reported symbols are called Mulliken Symbols (or Crystal Field Term Symbols) and describe the global quantum state of the outer electrons population in a crystal. The left superscript is the spin multiplicity: 4 identifies a quartet state while 2 describes a doublet state. The spin selection rule states that electrons should not change their spin during a photon absorption, so transitions conserving the spin multiplicity are much more probable and are called "spin-allowed" whereas absorptions that lead to a change

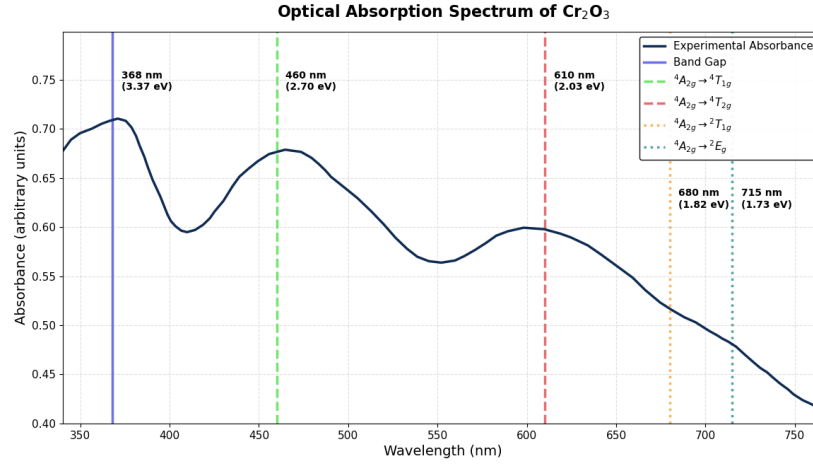


Figure 4.5: Experimental optical absorption spectrum of Cr_2O_3 . Apart from the direct band gap at 3.37 eV, intra-band electronic transitions are highlighted. Adapted from [57].

in spin multiplicity are much less intense and are called "spin-forbidden" transitions. Furthermore, the capital letter identifies the orbital degeneracy (A for singly, E for doubly and T for triply degenerate orbitals). Finally, the subscript number and letter denote the rotational symmetry and the parity [70].

4.1.4. Manufacturing and Annealing of Chromium Thin Films

Before considering any engineering application of chromium coatings, it is important to establish a deep understanding of their fundamental structural, mechanical, and thermal properties. Since the protective efficacy of a chromium-based coating strictly depends on its capability to generate a robust Cr_2O_3 scale, this section reviews the literature following a logical two-step sequence. First, it investigates the oxidation kinetics of metallic chromium films in high-temperature environments, which is fundamental to predicting how the protective scale forms. Secondly, it reviews the effects of high-temperature annealing on already formed chromia layers. Understanding this latter aspect is mandatory, as prolonged thermal exposure governs the healing of lattice defects, stress relief, and the long-term structural integrity of the oxide layer.

In recent years many studies emerged, addressing properties of Cr thin layers and their behavior in oxidizing atmospheres. Khojier et al. [52] investigated the structural and mechanical properties of chromium oxides formed by the thermal oxidation of pure chromium thin films deposited on Si wafers via Direct Current (DC) magnetron sputtering. Lower annealing temperatures (200–300 °C) generated a Cr_3O phase characterized by small grains and higher hardness. Higher temperatures (500–600 °C) produced Cr_2O_3 phase, but these

films exhibited lower hardness [52]. For annealing temperatures above 450 °C, Stierle et al. [71] observed a roughening of the formed oxide due to imbalance between the vertical diffusion of metal ions through the oxide and lateral diffusion across the surface. Mouche et al. [72] evaluated the characteristics of pure chromium coatings deposited via High Power Impulse Magnetron Sputtering (HiPIMS) on SiC substrates, and compared them with coatings produced using Cathodic Arc deposition (CA). HiPIMS technique (which will be analyzed in detail in the subsequent chapters) produces highly adherent films with superior hardness and crack resistance.

Complementary to these works, many campaigns explored the effects of high temperature-oxidizing exposure of chromium/chromia thin films. In a paper published by Auguste et al. [73], a multimodal approach was used to investigate point defects evolution in the Cr_2O_3 produced by thermal oxidation of pure Cr samples. The annealing experiments, carried out in air at 700°C, proved that defects concentration decreased as annealing time increases, while adherence and stability of the growing chromia layer was confirmed. Khalaf et al. [68] confirmed the reduction of disorder and defects via thermal annealing on Radio Frequency Magnetron Sputtering deposited chromia films. Dorcheh et al. [74] observed that spallation of thermally grown chromia scales often occurs during cooling process, due to large compressive stresses generated within the oxide scale. All the consulted studies agree on the fact that thermal annealing improves the adhesion of coatings to the substrate, due to relief of deposition stresses and interdiffusion at the film-substrate interface [75, 74].

The comparative analysis of these deposition methodologies, ranging from RF/DC Magnetron Sputtering [68, 52] and E-beam Evaporation [76] to Cathodic Arc Ion Plating [72], highlights a significant divergence in coating performance. HiPIMS emerges as the most suitable technique for the manufacturing of anticorrosive barriers. Thanks to the superior energy given to the deposited species, it allows the formation of ultra-dense, pore free coatings with exceptional adhesion and high resistance to crack propagation (thanks to the inherent compressive stress state).

Despite the advancements in the field, a comprehensive understanding of the oxidation kinetics of chromium coatings deposited via HiPIMS remains unexplored. Consequently, understanding how these coatings evolve into protective Cr_2O_3 scales during controlled thermal treatments is a mandatory prerequisite for their deployment in LFRs. Building on this necessity, the first part of the experimental work focuses on investigating the thermal oxidation of HiPIMS-deposited Cr films via a systematic air annealing campaign, aiming to fill this research gap and optimize the barrier for subsequent liquid lead exposure.

4.2. State of the Art: Chromium Coatings in Nuclear Environments

4.2.1. Chromium Coatings for ATF

As introduced in Section 1.3.1, the accident of Fukushima further underscored the pre-existing need for the development of advanced ATFs for LWRs [13]. While in the early stages some ATF concepts involved replacing Zircaloy with innovative materials like monolithic FeCrAl or SiC composites, applying a protective surface coating to the existing Zircaloy substrate has emerged as the most promising, near-term deployable solution [77, 13]. This approach is highly favored because it lowers R&D costs, is compatible with existing fuel manufacturing infrastructure and, most of all, does not compromise the reactor operation (given the low interference with thermomechanics and neutronics) [47].

Many works emerged in the last decade, which confirm the effectiveness of chromium coatings in reducing Zircaloy oxidation in high temperature steam environment [47, 77, 78]. In a recent study, Yang et al. [78] reported that Cr coatings enhance the overall performance of Zircaloy cladding tubes and, the protective layer, shows great adherence to the substrate even in the most severe accidental conditions. Liu et al. [47] systematically studied the degradation mechanisms of Cr-coated Zircaloy-4 under isothermal steam oxidation at 1200 °C, proving the excellent performance of the coating produced with magnetron sputtering. This study identified the cause of the failure after long exposure: Zr outward diffused through the Cr layer, causing the reduction of the outer scale of Cr_2O_3 to Cr. Moreover, Song et al. [13] highlighted that Zr-Cr interdiffusion triggers eutectic melting at 1332 °C, setting an upper bound for the coating thermal resistance. To address this critical challenge bilayer coatings were developed, in which a Mo interlayer blocks the interdiffusion of Cr and Zr. Aronson et al. [77] investigated the microstructural optimization of chromium coatings deposited via cathodic arc physical vapor deposition. The study demonstrated that compact and defect-free films are much more effective. Furthermore, the paper by Kim et al. [79] evaluated the effects of 1.5 μm chromium coating deposited via DCMS. Surprisingly, the thermal performances were significantly enhanced by the coating even after oxidation, exhibiting a Critical Heat Flux (CHF) enhancement of nearly 50%. In their recent work, Wang et al. [80] compared the microstructural and mechanical performance of chromium coatings deposited via HiPIMS against traditional DCMS. The study demonstrated that HiPIMS process effectively suppresses the growth of coarse columnar crystals which are typical of DCMS, yielding a highly refined, dense, and compact morphology. Consequently, this microstructural refinement endows the HiPIMS-deposited

coatings with superior hardness, higher compressive residual stresses, and a significantly enhanced fatigue life.

The extensive volume of research conducted in high-temperature steam environments unequivocally demonstrates the exceptional barrier effectiveness and thermo-mechanical stability of chromium coatings under extreme conditions. Crucially, their ability to rapidly grow a dense, continuous, and highly adherent chromia scale not only halts the inward diffusion of oxygen in LWRs, but also presents the physical and chemical properties required to block the outward dissolution of vulnerable substrate elements (such as Ni and Fe) into Heavy Liquid Metals. Building on this proven potential, the following section will review the state of the art of chromium coatings in liquid lead and lead-bismuth environments, ultimately identifying the critical research gaps that motivate the experimental work of this thesis.

4.2.2. Chromium Coatings for LFRs

In recent years, many experimental campaigns were carried out, a large variety of materials was tested and chromium based coatings were highlighted among the most promising solutions to LMC and LME in LFRs [28].

Many studies focused on the behavior of FeCrAl-based alloys. Galli De Magistris et al. [81] investigated the corrosion of FeCrAlNi metallic coatings on 316L steel in liquid lead at 600°C. The films, produced with HiPIMS, performed well and after 1000 h of exposure, combined with irradiation, no significant corrosion was observed. Fetzner et al. [82] focused on the performance of modified FeCrAlY coatings deposited with Low Pressure Plasma Spray on T91 steel. Exposed to oxygen-containing lead at 500°C, the substrate was successfully protected. The presence of at least 10% of Cr proved vital to assist the formation of a protective oxide scale. Weisenburger et al. [46, 83] extensively evaluated the performance of GESA (Gepulste ElektronStrahl Anlage)-modified FeCrAlY coatings under severe reactor-relevant conditions. By subjecting the coated cladding tubes to temperatures up to 600 °C, flowing LBE, and internal pressurization to simulate fuel swelling, they demonstrated the exceptional stability of these surface modifications. The FeCrAlY layer successfully developed a highly protective alumina scale that withstood both high-speed LBE erosion and stress-induced accelerated oxidation. In a recent review, Yu et al. [84] highlighted the formation of a dense Cr_2O_3 scale after the exposure to lead of FeCrAl-based High Entropy Alloy. The absence of signs of LMC demonstrated the crucial role of chromia in inhibiting elemental dissolution. Furthermore, Liu et al. [85] produced a comparative study on the intrinsic LBE corrosion resistance of pure Cr_2O_3 , ZrO_2 and

Mn_3O_4 . Chromia outperforms both Zr and Mn oxides in LBE environments. It exhibited a lower oxidation rate and remained highly dense and structurally stable without cracking at 600°C and 700°C. First-principles calculations confirmed that Pb, Bi and O have the lowest diffusion coefficients in chromia (compared to the other two oxides).

The selection of chromium as a primary candidate is further supported by a recent work by Wang et al. [54]. In their investigation, pure Cr layers were deposited on T91 and SIMP steels via RF Magnetron Sputtering. The coatings, 3 μm thick, were exposed to static, oxygen-saturated ($C_O \approx 10^{-3}$) LBE at temperatures of 600°C and 700°C for a maximum of 300 h. Coatings reacted with the dissolved oxygen to form a dense and continuous Cr_2O_3 layer about 4 μm thick. This layer showed great stability, efficiently hindering LMC for the tested conditions. No signs of structural damage or spalling off were detected, confirming the compatibility of the thin chromium layers with the substrate.

Despite the demonstrated potential of pure Cr/ Cr_2O_3 coatings in inhibiting liquid metal corrosion, just a restricted number of experiments have been conducted to test the actual effectiveness of such anticorrosive films in liquid lead environment. To expand the understanding in this field, the second part of this thesis work proposes a novel approach to LMC mitigation featuring metallic chromium coatings deposited via HiPIMS.

4.3. Summary and Thesis Goals

The preceding chapters have addressed the fundamental concepts required to frame this work and motivate the research objectives. In Chapter 1 the principles of nuclear fission physics and the current global status of nuclear power production were presented, highlighting the necessity of a new generation of nuclear power plants. Subsequently, in Chapter 2 the Lead-Cooled Fast Reactors are introduced, with a focus on the global research landscape. From this analysis, the need for the development of novel strategies for LMC mitigation emerges as the principal concern hindering the deployment of these reactors. Chapter 3 delves into the details of the phenomena causing material degradation in lead-facing components, reviewing the factors which make this environment so challenging. The outcome of this chapter is the need of further development of effective mitigation strategies, with anticorrosive coatings standing out as the most promising near-term solution. Notably, chromium represents an established protective material due to its capability of growing stable and dense Cr_2O_3 scales when exposed to oxidizing environments. Finally, chapter 4 provides a review of nuclear applications of anticorrosive chromium coatings, aiming to identify the research gap that this work intends to fill.

While pure chromium is established as a premier candidate for ATF applications, the liter-

ature lacks studies investigating the behavior of such technology under LFR-relevant corrosive conditions. Furthermore, various deposition techniques have been tested for the production of thin films, among which HiPIMS has demonstrated technical superiority. However, no studies are available regarding the oxidation kinetics of HiPIMS-deposited metallic chromium coatings. Additionally, the effectiveness of HiPIMS-deposited chromium coatings in mitigating LMC has yet to be tested.

The primary objective of this thesis is to characterize and validate a novel chromium-based anticorrosive barrier for LFR applications. This goal is pursued through a two-step approach. First, the high-temperature behavior of HiPIMS-deposited chromium layers in oxidizing environments is investigated to quantify their structural evolution. This preliminary study aims to determine whether controlled thermal annealing can effectively serve as a mechanism to grow dense, highly crystalline oxide scales. The knowledge gained from this oxidation campaign is exploited for the optimization of the protective bi-layer architecture and provides fundamental insights to interpret the degradation mechanisms observed later. Finally, the research aims to evaluate the effectiveness of this engineered barrier by assessing its corrosion resistance in a stagnant liquid lead pool under LFR-relevant conditions.

The coating engineered in this work consists of a bi-layer architecture:

- **Internal pure chromium layer:** Deposited directly onto the steel substrate's surface via HiPIMS. A nominal thickness of 1 μm was selected for this interlayer to mitigate excessive thermal stress accumulation arising from differential thermal expansion with respect to the steel substrate, while simultaneously guaranteeing a sufficient chromium reservoir.
- **External Cr_2O_3 layer:** Grown over the underlying Cr film via controlled thermal annealing in an ambient air atmosphere. Growing a high-quality chromia scale before liquid metal exposure offers a robust strategy to contrast the low oxygen potentials within the liquid lead, which could inhibit the passivation of the bare chromium coating.

This bi-layer structure is designed to combine the advantages of both inert-ceramic and metallic coatings. The underlying chromium layer should act both as an interlayer improving adhesion and compatibility with the substrate, and as a chromium reservoir that confers self-healing capability to the external Cr_2O_3 scale.

Accordingly, this research aims to answer the following fundamental questions:

1. How do HiPIMS-deposited metallic chromium thin films evolve structurally when

subjected to high-temperature oxidizing environments?

2. What are the physical and structural properties of the resulting thermally grown oxide scales?
3. What are the optimal thermal annealing parameters required to engineer a robust and highly protective bi-layer architecture?
4. How does the engineered Cr/Cr₂O₃ barrier perform when exposed to an LFR-relevant stagnant liquid lead environment?

4.3.1. Methodological Approach

To effectively answer the formulated research questions, the experimental work was structured as follows:

- **Controlled Thermal Oxidation.** Pure chromium coatings, previously deposited on Silicon substrates via HiPIMS, underwent a controlled thermal oxidation campaign in a muffle furnace. This step was designed to investigate the high-temperature oxidation kinetics of the films and assess the fundamental properties of the grown chromia scales.
- **Microstructural Characterization.** The structural and morphological properties of the thermally grown oxide were quantified using Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDXS), and multi-wavelength Raman spectroscopy. This analysis constituted a fundamental investigation into the intrinsic properties of the chromia scales, and its findings were subsequently exploited to select the optimal annealing parameters for the final barrier development.
- **Liquid Lead Corrosion Testing.** To assess the protective capability of the coatings and identify their degradation mechanisms, the optimized architectures were tested in an oxygen-containing stagnant liquid lead pool within the CAPSULE facility at the ENEA Brasimone Research Center.

The combination of these techniques enabled a comprehensive investigation of coating oxidation and corrosion behaviour. In the following chapter, the aforementioned methods are explained in detail, describing the specific setups used and providing insights into how they contributed to this work.

Part II

Methods

5 | Production and Oxidation of Chromium Coatings

This chapter details the processes employed to develop the chromium-based bilayer coatings. It provides a comprehensive overview of the experimental setups used, beginning with the High-Power Impulse Magnetron Sputtering (HiPIMS) technique for the deposition of the metallic chromium films. Subsequently, the chapter outlines the experimental configuration used for the controlled thermal annealing treatments performed in a muffle furnace.

5.1. High-Power Impulse Magnetron Sputtering

As mentioned in Part I, in order for protective coatings to act as effective diffusion barriers to halt corrosion, specific requirements such as high density, thermal and chemical stability, good adhesion and mechanical properties must be met. Magnetron Sputtering (MS) is a Physical Vapour Deposition (PVD) technique well-suited for this kind of application. In particular, High-Power Impulse Magnetron Sputtering (HiPIMS) was used for the deposition of chromium coatings involved in this work [86, 87].

Physical sputtering is the erosion process of a surface induced by the bombardment of heavy plasma ions [88]. In fact, if a particle hits the surface of a given material and manages to transfer enough energy to the target atoms, ejection of such atoms will occur. This can be exploited to vaporize a target and generate a flux of sputtered species to be deposited [89].

For the deposition of thin films, the simplest way to exploit physical sputtering is to continuously sputter a target material through an ionized working gas (often argon). In the configuration reported in Figure 5.1a, an electrostatic potential is applied between the electrodes to generate a glow discharge, ionizing part of the gas atoms. These are consequently accelerated by the electric field towards the cathode, impacting on the target surface [90]. If the transferred energy overcomes a certain threshold, a series of collisional

events leads to the ejection of neutral atoms and secondary electrons (which are fundamental for the glow discharge to become a self-sustained process) [91]. Sputtering yield is defined as the mean number of target atoms ejected per single incident bombarding particle. The ejected species diffuse through the high-vacuum chamber and condense on the substrate producing characteristic columnar structures. The configuration in which a Direct Current (DC) power supply is connected to the cathode is called DC diode sputtering [90].

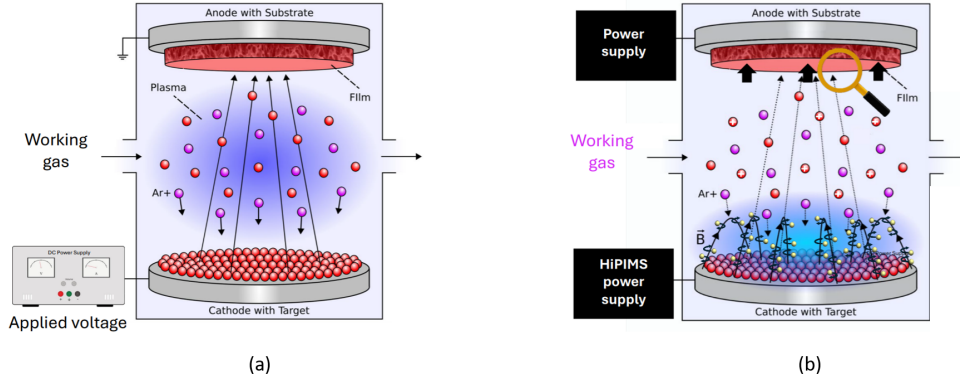


Figure 5.1: Schematic representation of (a) DC diode configuration and (b) HiPIMS with negative bias voltage applied to the substrate configuration. Adapted from [91].

While relative simple, DC diode sputtering has severe limitations in terms of operating pressures and deposition rates. In fact, to sustain the glow discharge it is necessary to have pressures of 2 Pa to 4 Pa in the chamber, causing high interaction between the sputtered species diffusing to the substrate and the working gas. This limits the deposition rate to 10s nm/min [91].

Performances of sputtering deposition can be enhanced by increasing the electrons residence time near the target using suitable permanent magnets positioned below the cathode (as visible in Figure 5.1b). As a result, the ionization efficiency increases and lower gas pressures (well below 1 Pa) and voltages (hundreds of V compared to a few kV for diode configuration) can be used. When the use of such permanent magnets is combined with DC power supply, the deposition technique takes the name of DC Magnetron Sputtering (DCMS) [91]. In general, a high ion fraction of the sputtered species is beneficial for the film growth since the substrate can be biased with negative voltage to accelerate ionized particles towards the growing film. As the energy of the deposited particles increases, the quality of the process improves, producing more compact films also on more complex geometries. However, DCMS technique is limited by a low ionization of the sputtered species (below 1 %) [92].

Massive improvements in the ion fraction can be obtained with increased plasma density and, in the 1990s, it was observed that due to the self-sustaining nature of the magnetron discharge, higher plasma densities could be reached by providing more power to the system [93]. Unfortunately, above tens of W cm^{-2} the target starts to overheat. To overcome this limit, it is possible to add to the DC power supply a pulser, which can quickly turn on and off the cathode voltage. The resulting technique takes the name of High-Power Impulse Magnetron Sputtering (HiPIMS). Short (tens to hundreds of μs) pulsed plasma discharges with high power (some kW cm^{-2}) but low duty cycle (between 0.5 % to 5 %) are typically exploited in configurations like the one reported in reported in Figure 5.1(b). Experimentally it can be shown that electron plasma density in HiPIMS plasma can reach 10^{18}m^{-3} resulting in an ion fraction of the sputtered species above 70 %. The main drawback of HiPIMS configuration is the phenomenon of self-sputtering: the ionized emitted atoms of the target can be re-accelerated towards the target with detrimental effects for the deposition rate (already negatively affected by the low duty cycle of this operating mode). Despite this disadvantage, the high energy imparted to the deposited species in the HiPIMS configuration (with bias voltage applied to the substrate) activates recrystallization processes and suppresses columnar growth. The resulting films exhibit a dense, homogeneous microstructure coupled with excellent hardness and interfacial adhesion, which are the critical functional requirements of a candidate anticorrosive barrier.

5.1.1. Experimental Deposition Setup

All chromium depositions used for this work were produced using the custom experimental setup provided by the Micro and Nanostructured Material Laboratory (NanoLab) at Politecnico di Milano. This setup, capable of both DCMS and HiPIMS depositions, consists of a vacuum chamber, a vacuum system (pumps and pressure gauges), a direct current power supply and a pulser.

The deposition chamber is a cylindrical steel chamber, internally covered with a detachable aluminum cover that permits periodic cleaning of the walls from impurities. Inside the chamber (shown in 5.2), the substrate holder is located in the upper region and can be negatively biased relative to the anode (the grounded chamber walls) to perform biased depositions. A motor can impose rotation to the substrate (up to 20 rpm) to improve deposition uniformity; a resistive system allows heating of the substrate up to 400°C . In the lower part of the chamber, two water-cooled cathodes are located, each of them hosting a 3-inch magnetron target in confocal geometry. The system is powered through two DC generators of 6000 W and 1500 W connected to a pulsing module. The pulser enables to set the on-time and the off-time of the cathode voltage, defining the system's

duty cycle.

The pumping system features a primary rotary pump and a turbomolecular pump. The standard pumping procedure starts with the primary pump bringing the chamber down to 8 Pa and, when this pre-vacuum condition is reached, the turbomolecular pump reduces the pressure down to $5 \cdot 10^{-5}$ Pa. Once the desired pressure is reached, argon is introduced in the chamber. Its mass flow is controlled through a feedback system to maintain the desired gas pressure. The vacuum diagnostics system consists of two Pirani gauges (minimum pressure $5 \cdot 10^{-2}$ Pa), a Pirani-Ion gauge (minimum pressure $5 \cdot 10^{-8}$ Pa) and a capacitance gauge with 10 Pa full-scale.

The discharge can be monitored visually from a window in the steel chamber or with a digital optical spectrometer attached to the window.



Figure 5.2: Image of the components inside the vacuum chamber of the HiPIMS setup.

In Table 5.1 the process parameters and the characteristics of the deposited chromium coatings studied in this work are reported. Such deposition parameters were optimized in previous works by other group members to maximize density and stiffness of the deposited coatings.

Table 5.1: Experimental deposition parameters optimized for the High-Power Impulse Magnetron Sputtering (HiPIMS) deposition of the chromium coatings.

Deposition Parameter	Value
Pulse length	100 μ s
Bias	150 V

5.2. Annealing Furnace

The oxidation experiments were carried out using an electric muffle furnace, capable of reaching up to 1000 °C. The work by Massari [94] done at NanoLab research group, demonstrated that thermal annealing of HiPIMS-deposited chromium coatings analogous to those of the present study, in air, produces pure Cr_2O_3 phase for temperatures above 500 °C. Moreover, at temperatures exceeding 600 °C compatibility problems between the chromium film and the silicon substrate were highlighted. For these reasons this thesis work focuses on the comprehensive characterization of the oxidation kinetics at temperatures between 500 and 600 °C. In order to investigate such phenomenon, exposures to high temperature oxidant environment were conducted for times between 1 and 10 hours. Table 5.2 summarizes the thermal annealing conditions investigated in this work.

Table 5.2: Summary of the investigated annealing parameters.

Annealing Temperature	Dwell Durations (h)			
500 °C	1	3	5	10
550 °C	1	3	5	10
600 °C	1	3	5	10

During all the annealing experiments the samples were heated with a temperature increase rate of 4 °C/min. This slow heating rate is needed to avoid excessive stress accumulation due to mismatched thermal expansion coefficients between the coating and the substrate. Similarly, when the dwell time finished, the specimens were left inside the muffle furnace until the temperature dropped below 50 °C via slow natural cooling.

6 | Characterization Techniques

This chapter presents the experimental techniques and the setups utilized to analyze the structure and composition of the manufactured coatings. Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDXS) were employed for microstructural characterization and the determination of elemental distribution. Following this, the chapter explains Raman and Photoluminescence spectroscopy, detailing how these non-destructive techniques are utilized to probe the crystalline structure, evaluate residual stresses, and investigate the presence of defects within the thermally grown oxide scales.

6.1. Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

Scanning Electron Microscopy is a technique that enables the acquisition of high-resolution images at micro- and nanometric scales. In a Scanning Electron Microscope (SEM), a beam of electrons is used to probe the analyzed surface. The use of electrons accelerated to tens of kV permits overcoming the intrinsic resolution limit of optical microscopes. In fact, the latter exploits visible light whose associated wavelength is hundreds of nm and this gives rise to an intrinsic resolution limit imposed by diffraction phenomena. Using electrons, whose De Broglie wavelength depends on the accelerating voltage and can reach nanometric values, it is possible to resolve nanometric features and thus produce high resolution images. A schematic representation of the SEM is shown in Figure 6.1.

Electrons are generated via thermionic effect by heating to high temperature a tungsten filament in a vacuum chamber; subsequently they are collimated and accelerated by an electrostatic voltage ranging from 0.3 to 30 kV and, once the sample is reached, multiple phenomena can occur. Primary electrons can undergo elastic scattering and the so-called backscattered electrons (BSE) can be detected and used for image reconstruction. Secondly, inelastic scattering with the material is possible, causing the emission of secondary electrons (SE) and of characteristic x-rays. SE can be exploited for imaging too: compared to BSE, secondary electrons are more sensitive to shadowing effects providing the

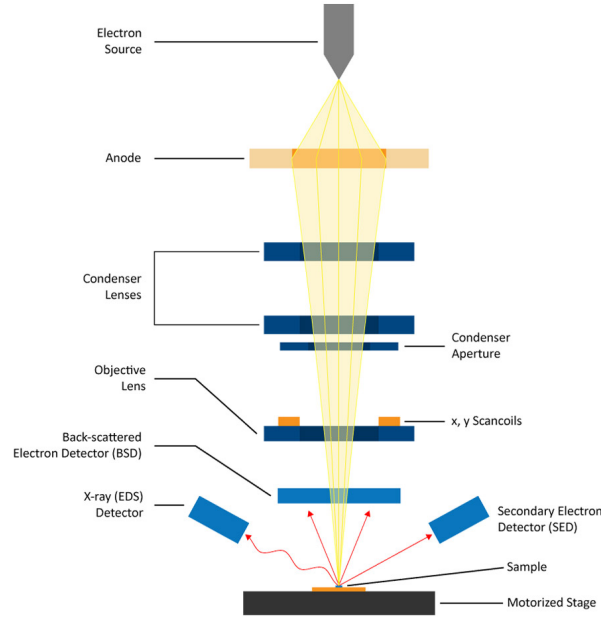


Figure 6.1: Schematic of a scanning electron microscope [95].

reconstructed images with a 3D appearance. On the other hand, backscattered electrons produce images where heavy elements produce a brighter signal, since the scattering cross section depends on Z^2 and thus providing qualitative information about sample's composition.

The X-rays emitted by the sample can be exploited to extract quantitative information about the sample's composition. Such photons, coming from the de-excitation process of atoms which underwent inelastic collisions with the electrons from the gun, are acquired using a photon detector and from their energy it is possible to reconstruct the elemental composition of the sample. This analytical technique is called Energy Dispersive X-ray Spectroscopy (EDXS) and was used to produce maps and linescans describing the elemental distribution of the observed specimens.

The SEM used in the present study is a Zeiss Supra 40 field-emission scanning electron microscope with a Gemini column, equipped with an Oxford EDXS spectrometer, a BSE detector and a SE detector. X-rays are collected with a solid-state silicon detector with energy resolution of 10 eV. The selected accelerating potential for the electrons was 10 kV.

6.2. Raman Spectroscopy

Raman spectroscopy is a non-destructive technique used in material science to investigate the vibrational properties of crystals [96]. This technique provides detailed information on the vibrational properties of materials. It is widely employed to investigate crystalline phases, residual stresses, structural disorder, defects, and microstructural evolution and is particularly suitable for the analysis of thin films. In this study, Raman Spectroscopy, using different excitation wavelengths, has been extensively used to assess the properties of the oxidized chromium films and for the post-exposure analysis of corroded samples. Alongside Raman spectra, with the same experimental setup, it was possible to collect the photoluminescence spectra excited at the selected wavelength, providing deeper insights into the structural and electronic evolution of the growing oxide scales. In the following section a theoretical description of these two effects is given and, subsequently, the experimental setup used for this study is described.

6.2.1. Theory of Raman Scattering

Raman spectroscopy is based on the physical phenomenon of inelastic photon-phonon scattering. When visible light (emitted from a monochromatic laser source) impinges on the surface of a crystalline material, the incident photons interact with the local electronic cloud and the lattice vibrations. The resulting scattered radiation yields a spectrum containing a strong peak at the same frequency as the incident light ω_L (representing elastic scattering of the incident light, namely Rayleigh scattering) and a pair of weaker lines at the frequencies $\omega_L \pm \omega_j$. The weaker lines are generated by the inelastic phonon-photon interaction and the frequency ω_j is the frequency associated to the interacting phonon. Two possible inelastic mechanisms are possible: Stokes Raman scattering takes place when the photon gives energy to the lattice and a photon with lower energy is emitted; anti-Stokes Raman scattering occurs when the lattice relaxes from an excited vibrational state to a lower one, emitting a photon with higher energy. As shown in Figure 6.2, normal non-resonant Raman effect, the system is not promoted to a real electronic state; instead, the interaction is instantaneous, exciting the system only to a virtual energy level [97].

Since at room temperature most of the vibrational modes of the crystal are at ground state (phonons distribution is ruled by Bose-Einstein statistics), the intensity of Stokes line is much larger than that of the anti-Stokes one: this is the reason why Stokes peaks are the ones analyzed in Raman spectroscopy [97].

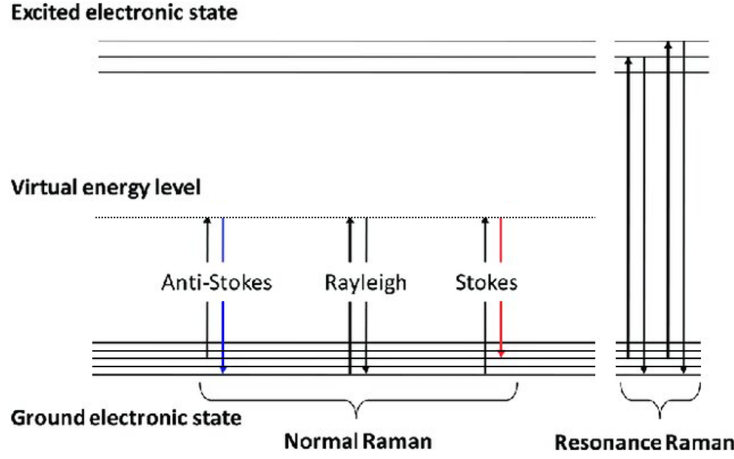


Figure 6.2: Schematic representation of the transitions associated to photon-phonon interaction [98].

It is fundamentally important to recognize that Raman spectroscopy cannot reveal every lattice vibration, as the phenomenon is strictly governed by physical and symmetry-based selection rules. The wave vector k_L associated with the incident light in the visible range is much smaller than the parameter $\frac{\pi}{a}$ defining the boundary of the first Brillouin zone; consequently, momentum conservation restricts observable scattering events to phonons located at the center of the first Brillouin zone. Because acoustic phonons possess zero frequency at this critical symmetry point, Raman scattering is strictly limited to optical phonons [97]. Furthermore, not all optical vibrational modes of a structure are observed: only those satisfying specific symmetry requirements associated to the macroscopic polarizability tensor produce a detectable Raman signal. The resulting collection of Raman peaks produces a characteristic fingerprint unique to each specific material phase and stoichiometry, as described in for chromia in Section 4.1.2. While most electrical insulators and semiconductors display a well-defined Raman fingerprint, electrical conductors such as bulk metals remain inherently Raman-silent. This absence of signal is governed by a combination of multiple phenomena, most notably the extremely limited optical penetration depth of visible light within highly reflective metallic media, as well as the fundamental absence of optical phonons in the monatomic primitive cells characteristic of most bulk metals.

Resonant Raman Effect

When the frequency ω_L of the excitation laser approaches a real electronic transition frequency, the intensity of the observed Raman bands is significantly enhanced, resulting in the so called resonant Raman effect in which the scattering cross section increases

by several orders of magnitude (typically up to 10^3 to 10^5). It is possible that this resonance involves only a group of peaks if the excited electronic transition involves only certain atoms, mostly vibrations associated with those specific atoms will be enhanced. This signal amplification is particularly useful when the spectrum is affected by high and noisy background, typical of thin-film architectures [97]. Finally, tracking Raman resonances with the use of multiple excitation wavelengths can indirectly probe the electronic structure of the sample, highlighting the possible electronic transitions.

Lasers in Raman Spectroscopy

As a high-intensity single frequency light source, laser is an ideal excitation source for Raman analysis. The choice of the photon wavelength associated to the laser can significantly influence the measurement due to resonance Raman effect and photoluminescence phenomena (that will be discussed later on). Furthermore, Raman cross section depends on the fourth power of ω_L , so lasers with higher ω_L will produce improved spectra, with better signal-to-noise ratio. Laser frequency also influences the penetration depth: in general the smaller the frequency, the higher the penetration depth. The laser power is another relevant parameter: since it can induce sample heating and even burning, it is advisable not to use very powerful lasers for Raman spectroscopy.

Alteration of Raman spectra

The position, width, and shape of the measured Raman lines often deviate significantly from those of standard bulk crystalline reference materials. Such spectral alterations can be driven by various physical phenomena:

- Residual stresses in the crystalline structure alter the equilibrium distance among atoms, causing variations to the frequency of the optical phonons [99, 60]. As an example, as reported in Section 4.1.2, the presence of compressive stresses in chromia crystal typically induce a displacement of the A_{1g} vibrational mode towards higher wavenumbers, with respect to the stress free reference value.
- Nanometric dimensions of crystallites allow for the Raman activity of non-zone-center phonon modes due to the disruption of perfect translational symmetry. Depending on the specific phonon dispersion relation, this phenomenon leads to line broadening and can cause either up or down shifts in the Raman wavenumbers. A similar effect is observed if the specimen contains some amorphous inclusions [62] or lattice defects, such as point impurities, vacancies, and disordered atomic bonds [100].

- Local warming of the sample can cause broadening of Raman lines [60]. Laser-induced heating can occur during spectral collection; therefore, limiting the incident laser power is crucial to prevent undesired alteration of the Raman peaks.

6.2.2. Theory of Photoluminescence

Photoluminescence (PL) is a process in which a material absorbs electromagnetic radiation, exciting one of its electrons to a higher electronic excited state, and then radiates a photon as the electron returns to a lower energy state. If the material dissipates in a non-radiative way part of the absorbed energy, the radiated photon is of longer wavelength than the absorbed photon. Fluorescence and phosphorescence are two forms of photoluminescence [101]. Given this definition, it follows that Raman lines and photoluminescence bands frequently overlap within the same spectral window. In materials science, PL spectroscopy provides crucial complementary insights into the optical and electronic properties of crystalline structures.

6.2.3. Experimental Setup

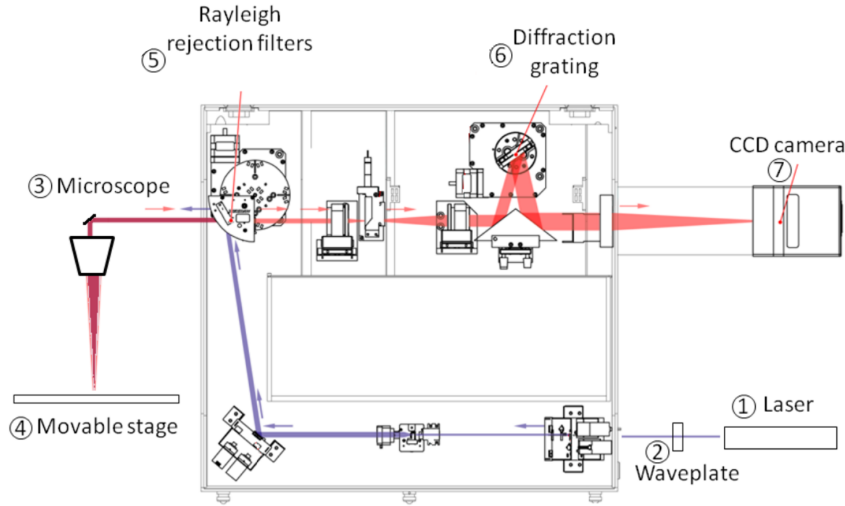


Figure 6.3: Layout of the Reinshaw InVia confocal Raman microscope. The incident light is represented by the purple lines, while the scattered light is represented by the red lines. Adapted from [102].

Most of the Raman spectra were collected using an InVia confocal Raman microscope. As shown in Figure 6.3, it consists of: (1) several monochromatic laser sources; (3) a microscope to shine the light on the sample and collect the scattered light; (4) a movable stage; (5) dielectric “edge” filters to cut the Rayleigh part of the spectra; (6) a diffraction

grating for dispersing the Raman scattered light; (7) a CCD camera for detecting this light. A grating with 1800 l/mm was used for all the measurements and a 100x objective was mounted on the microscope. This device offers two distinct acquisition modalities: the so called "static mode", wherein the diffraction grating is kept at a fixed angular position, is capable of rapidly collecting data in a range of around 2000 cm^{-1} for the utilized laser sources and an the "extended mode". The latter manages to collect signal in a range of 10000 cm^{-1} thanks to a continuous synchronized scanning of the grating. This second mode need longer acquisition time compared to static mode, but proved fundamental to collect photoluminescence spectra.

Multi-wavelength Raman characterization was conducted utilizing three excitation wavelengths. The 457 nm and 514 nm lines were supplied by an Argon-ion laser source, while a solid-state diode laser was employed to generate the 660 nm radiation. The power delivered to the sample was 0.5 mW for the green laser, 3.5 mW for the blue laser and 6.6 mW for the red one.

7 | Corrosion Tests

7.1. Corrosion Tests Facility

The corrosion tests were carried out utilizing the newly commissioned CAPSULE facility, constructed by *newcleo* and hosted at the ENEA Brasimone Research Center (shown in Figure 7.1). This experimental structure is designed to evaluate the corrosion characteristics of candidate structural steels and coatings.



Figure 7.1: CAPSULE facility at ENEA Brasimone research center. Adapted from [103].

Utilizing this infrastructure, *newcleo* is executing a rigorous screening aimed at qualifying high-performance materials for their next-generation Small Modular Reactors. It features 18 capsules filled with liquid lead and equipped with dedicated control systems to maintain temperature between 450°C and 750°C and oxygen concentrations between 10^{-8} wt% and 10^{-6} wt%. This configuration allows for materials to be tested under a wide range of conditions, as the facility can host 108 specimens simultaneously, supporting continuous and diversified experimental activities. Furthermore, CAPSULE is exploited also to study

coolant chemistry and to develop strategies for the continuous purification and monitoring of liquid lead [103].

For each capsule, an associated storage tank (2 liters capacity) is installed, to contain the liquid lead when no experiment is ongoing. Each capsule is internally aluminized and is equipped with a probe made of yttria-doped zirconia to monitor the dissolved oxygen concentration. The oxygen dissolved in the liquid Pb is controlled via a system which injects H_2 if oxygen content is above threshold or air if the oxygen content is too low. Ar is continuously injected for recirculation. Up to 6 samples can be exposed simultaneously in each capsule.

In this work, the lead parameters were set to be the most relevant conditions for the application in LFRs cores, so the specimens were exposed to liquid lead at 600 °C for 1000 h while the oxygen content was kept at 10^{-7} wt% throughout the experiment. During the exposure, samples are fixed to the extremity of a shaft through a screw. Figure 7.2 shows a sample right after extraction from the capsule.



Figure 7.2: Photo of a sample after exposure. Residual solidified Pb is covering the screw connecting the sample to the shaft.

After exposure, the samples' surface may be covered by liquid lead, which stuck to them during solidification. To facilitate the post-exposure analysis, a washing procedure is carried out using a solution capable of dissolving Pb and its oxides. Table 7.1 reports the chemical composition of such solution. Experimental evidence collected in the past highlighting that the washing procedure may alter the morphology of the sample and, for

this reason, for each tested coating two identical samples were exposed to corrosion, and only one was washed. In this way it was possible to analyze both washed and non-washed samples to investigate the effects of the procedure.

Table 7.1: Chemical composition of the solution utilized for post-exposure lead removal.

Chemical Component	Chemical Formula	Volume Fraction
Acetic acid	CH_3COOH	1/6
Ethanol	$\text{C}_2\text{H}_5\text{OH}$	1/6
Hydrogen peroxide	H_2O_2	1/6
Distilled water	H_2O	3/6

A total of two different novel chromium-based coatings were produced and tested in this thesis work. The rationale behind this choice, the specific features of these coatings, and the corresponding corrosion performance are detailed in Part III.

Part III

Results

8 | Characterization of Chromia Scales Thermally Grown on HiPIMS-Deposited Chromium Films

In this chapter, the first part of the experimental results will be presented and discussed. As anticipated in Section 4.3, the first phase of this work focuses on the morphological and structural characterization of thermally grown chromia scales on chromium thin films. The primary objective is to understand the oxidation kinetics of HiPIMS-deposited metallic chromium and evaluate its microstructural evolution in high-temperature oxidizing environments. This fundamental investigation was conducted entirely at the Micro- and Nanostructured Materials Lab (NanoLab) at Politecnico di Milano.

To pursue these objectives, this chapter presents a comprehensive investigation of the microstructural transformations occurring within HiPIMS-deposited metallic chromium coatings in high-temperature oxidizing environments. The study integrates a quantitative morphological characterization of the thermally grown chromia scales, focusing on their growth kinetics and grain size evolution. Furthermore, Raman spectroscopy is utilized to provide key insights into the phase composition and macroscopic residual stress state of the scales, while the application of different excitation wavelengths serves to highlight specific resonance effects. Concurrently, photoluminescence (PL) spectroscopy is employed as a complementary technique to qualitatively assess defect evolution and structural disorder across varying annealing conditions.

8.1. Morphological Characterization

This chapter directly builds upon the experimental findings detailed in the recent works of Sanna [104], Vaccari [105], and Massari [94]. Together, these studies comprehensively investigated the structural, morphological, and mechanical properties, as well as the oxi-

dation mechanisms, of chromium thin films deposited under various magnetron sputtering configurations. High Power Impulse Magnetron Sputtering (HiPIMS) emerged as the optimal deposition technique. Specifically, the application of a 150 V pulsed substrate bias produced films characterized by high density, low surface roughness, and the highest mechanical strength among the tested solutions. Furthermore, biased deposition was shown to delay microstructural degradation during high-temperature annealing, thereby demonstrating superior thermal stability. Massari identified the temperature range between 500 °C and 600 °C as the ideal window to grow compact Cr_2O_3 scales. This chapter deepens the investigation into the microstructural and vibrational phenomena occurring within this specific temperature regime, significantly expanding upon Massari's initial findings.

The chromium films utilized in this analysis were synthesized by colleagues within the NanoLab research group at Politecnico di Milano. Monocrystalline silicon substrates were chosen for the depositions as they do not influence the morphology of the deposited chromium film (given their extremely smooth surface) and can be easily cleaved for cross-sectional observation. Details about the deposition parameters exploited for the production of the 1 μm thick chromium films are reported in Section 5.1.

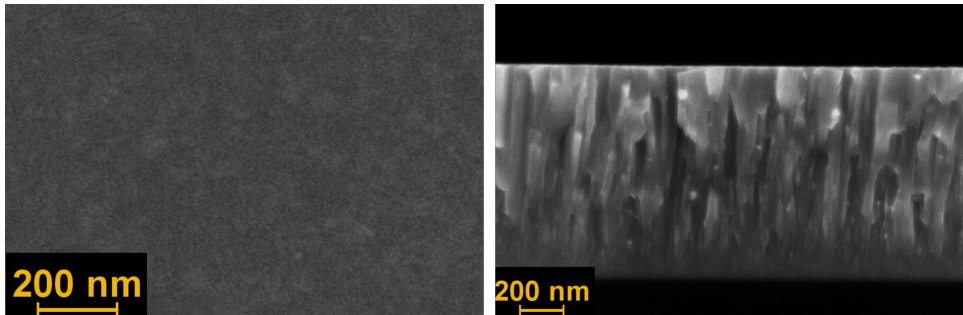


Figure 8.1: SEM images of planar and cross-sectional morphologies of the pristine metallic chromium film on silicon substrate.

Figure 8.1 illustrates the planar and cross-sectional microstructure of the pristine chromium coating. The high compactness of the film deposited with biased HiPIMS is evident from the cross section, alongside the optimal adherence of the film to the silicon substrate. Furthermore, it is possible to notice the low roughness of the surface, which appears very smooth in the planar image. These are the expected microstructural features of a high-quality coating deposited via biased HiPIMS [106]. Table 8.1 reports the quantitative properties of these chromium layers, as evaluated and provided by colleagues within the NanoLab research group. The measured density confirms, apart from the measure uncertainty, the high compactness of the film, as it closely approaches the theoretical value of bulk crystalline chromium (7.19 g/cm^3).

Table 8.1: Quantitative physical and chemical properties of the pristine HiPIMS-deposited chromium coatings.

Coating Property	Value
Thickness	929.95 nm
Uncertainty	2.30 nm
Density	7.32 gcm^{-3}
Uncertainty	0.37 gcm^{-3}
Oxygen content	0.69 Wt%

The planar and cross-sectional SEM images of the annealed samples are presented in Figures 8.2 and 8.3. For clarity, only the micrographs corresponding to the initial oxidation stage (1 h) and the mature scale (10 h) at each annealing temperature are shown to illustrate the morphological evolution of the chromia scale.

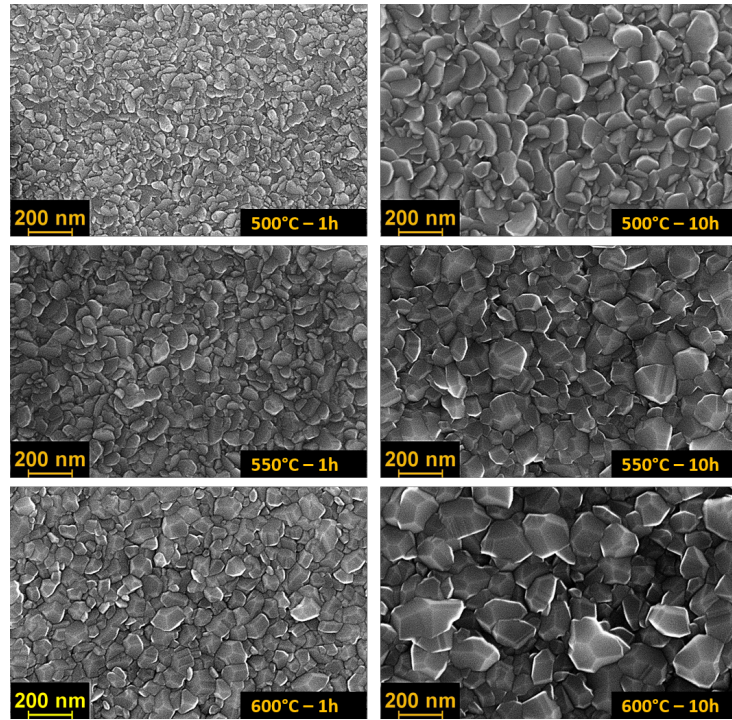


Figure 8.2: Surface morphology of the chromia scales thermally grown on HiPIMS-deposited metallic Cr films.

From the planar and cross sectional images of the sample annealed at 500 °C for 1 hour, it is clear that an oxide layer is already forming. The grains are in a nucleation phase, as the grain boundaries are not yet fully defined everywhere. As the annealing temperature and time increase, the grain size becomes progressively larger. At low annealing times, grains are more rounded and exhibit a uniform size distribution, whereas for longer annealing

8 | Characterization of Chromia Scales Thermally Grown on HiPIMS-Deposited Chromium Films

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times, the grains acquire a more polygonal and faceted shape, particularly at 550 °C and 600 °C. At extended annealing times and higher temperatures, the surface topography becomes three-dimensional. All chromia scales appear dense, with no macroscopic pores detected. Furthermore, no signs of cracking or spallation are observed on the surface.

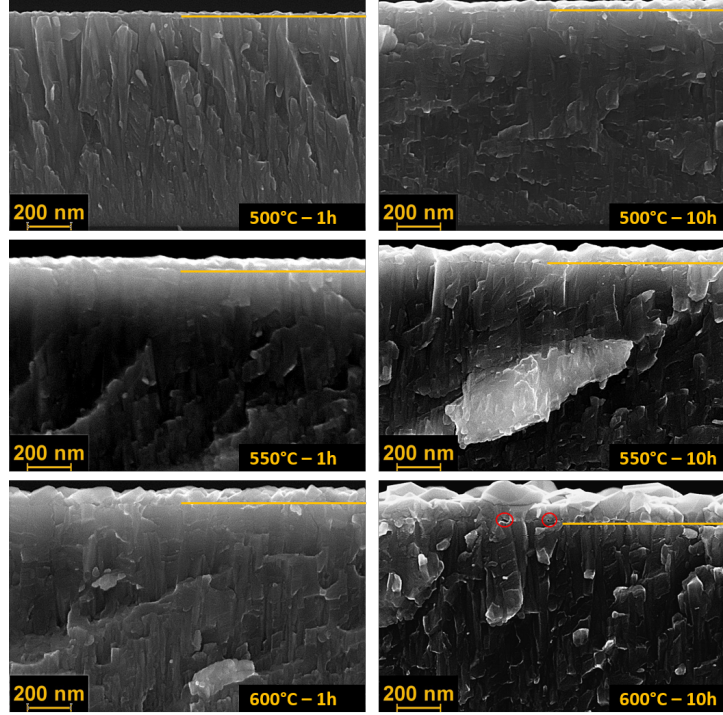


Figure 8.3: Cross-sectional morphology of the chromia scales thermally grown on HiPIMS-deposited metallic Cr films. Horizontal yellow lines highlight the interface separating metallic chromium and the oxide scale. Red circles indicate the presence of nanovoids in the sample annealed at 600 °C for 10 hours.

Observing the cross-sectional images in Figure 8.3, the oxide layers formed on top of the chromium films are clearly distinguishable, appearing nondamaged and adherent to the underlying metallic chromium in all the samples. A sharp boundary separates the oxide scale from the inner region of metallic chromium (indicated by the horizontal yellow lines), whose bulk morphology appears unchanged by the thermal treatment. These images confirm the outward growth of equiaxed grains, thicker oxide scales with increased surface roughness are observed for increasing annealing times and temperatures. The cross-sectional analysis also confirms that the oxide films are highly dense with no visible internal porosity, with the exception of the sample annealed at 600 °C for 10 hours. In this specific condition, nanometric voids are visible at the interface between the Cr_2O_3 scale and the metallic Cr, as highlighted by the red circles. Similar voids were observed in the work by Auguste et al. [73] and were attributed to the aggregation of vacancies that

collect at the metal/oxide interface during the oxidation process. The presence of such interfacial nano pores is consistent with enhanced diffusive mobility and microstructural rearrangements driven by prolonged oxidation. This phenomenon will be further discussed in the following sections.

In Figure 8.4a, the evolution of the oxide thickness is presented. Measurements of the scale thickness were performed manually from the SEM micrographs, utilizing multiple measurement points across the cross-section to ensure statistical reliability. The measured thickness of the thickest scale, formed via annealing at 600°C for 10 hours, is 125 nm ± 12 nm. The observed data appears to follow a kinetic evolution typical of oxidation processes primarily driven by ionic diffusion, suggesting a general agreement with Wagner’s theory of oxidation [107]. The observed profiles indicate a trend that is generally proportional to the square root of the annealing time, with the data being adequately described by the classical parabolic equation:

$$x^2 - x_0^2 = k_p \cdot t \quad (8.1)$$

Where k_p is the parabolic rate constant (often expressed in cm^2/s or nm^2/h), x is the oxide layer thickness, and t is the annealing time.

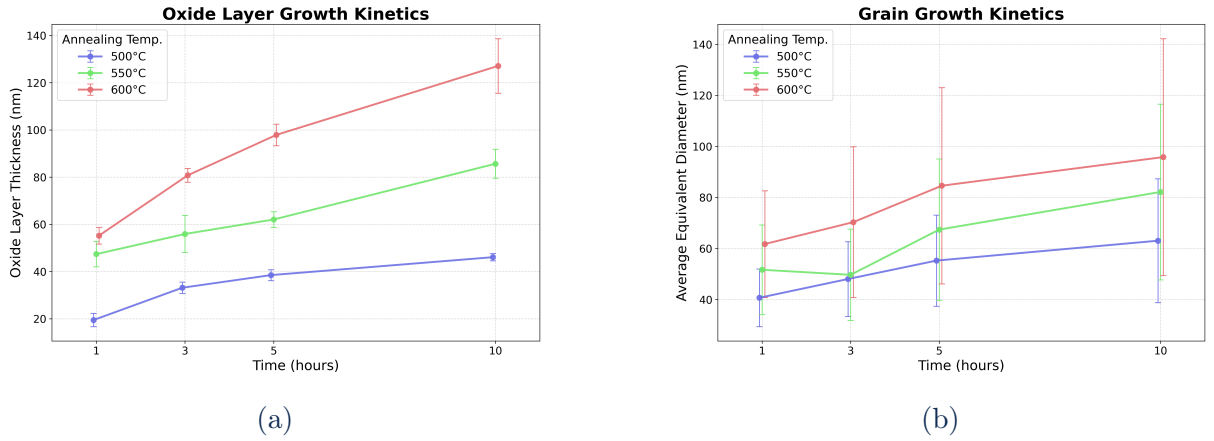


Figure 8.4: Oxidation and morphological growth kinetics of the chromia barrier evaluated at 500 °C, 550 °C, and 600 °C. (a) Progression of the oxide layer thickness. (b) Evolution of the mean equivalent grain diameter.

Using the Segment Anything Model (SAM), a machine-learning-based algorithm, it was possible to automatically segment hundreds of grains from the planar SEM micrographs to estimate the grain size distribution and the average grain size of each oxide scale. The resulting grain growth kinetics are plotted in Figure 8.4b. As expected for a thermally activated process, the mean grain size progressively increases with both annealing tem-

perature and exposure time. At 500 °C, microstructural coarsening is relatively slow, maintaining a fine oxide layer with average grain size of 63 nm after 10 hours. On the other side, at 600 °C, the higher thermal energy leads to an average grain size of 95 nm after 10 hours of thermal treatment. The error bars reported in the graph represent the standard deviation of the measured equivalent diameters distribution. Their increasing magnitude at higher temperatures and extended times reflects the physical broadening of the grain size distribution. This supports the visual observation that grain dimensions become increasingly heterogeneous as the oxide scale matures. This evidence is particularly important since, as reported by Kemdehoundja et al. [64], the total surface of grain boundaries is inversely proportional to the square of the mean grain size. The extension of grain boundaries surface has a direct impact on mechanical properties of the oxide scales and on the creep behavior of the scale: as the grain size increases, creep coefficient decreases and consequently the capability of the oxide scale of accommodating thermal stresses is expected to worsen [64]. Further details about thermal stresses are given in the next section.

8.2. Raman Analysis

Following the morphological characterization, which confirmed continuous growth of a dense scale, Raman spectroscopy was employed to verify the phase composition of the oxide, evaluate its structural integrity, and quantify the macroscopic residual thermal stresses developed within the film.

Figure 8.5 presents the Raman spectra collected utilizing the 514 nm (green) excitation wavelength. Consistent with the approach in Section 8.1, only the spectra of the most representative samples are reported to illustrate the evolution of the chromia scale's Raman signal. As the annealing time and temperature increase, the spectra become progressively more defined, revealing all the characteristic sharp peaks associated to active phonon modes of Cr_2O_3 listed in Table 4.2b. At the earliest oxidation stage (500 °C for 1 h), the acquired spectrum exhibits a low signal-to-noise ratio, with only the prominent A_{1g} peak being clearly distinguishable. Conversely, for the more mature scales, the complete Raman fingerprint of chromia is fully resolved. These measurements corroborate the findings of Massari [94], confirming that the oxidation of chromium above 500 °C exclusively yields the Cr_2O_3 phase, and that harsher annealing conditions promote improvement of the crystalline quality of the formed scale.

Crucially, the poor spectral quality of the 500 °C, 1 h sample must not be misinterpreted as a lack of crystallinity. The detection of the A_{1g} fundamental lattice mode proves that

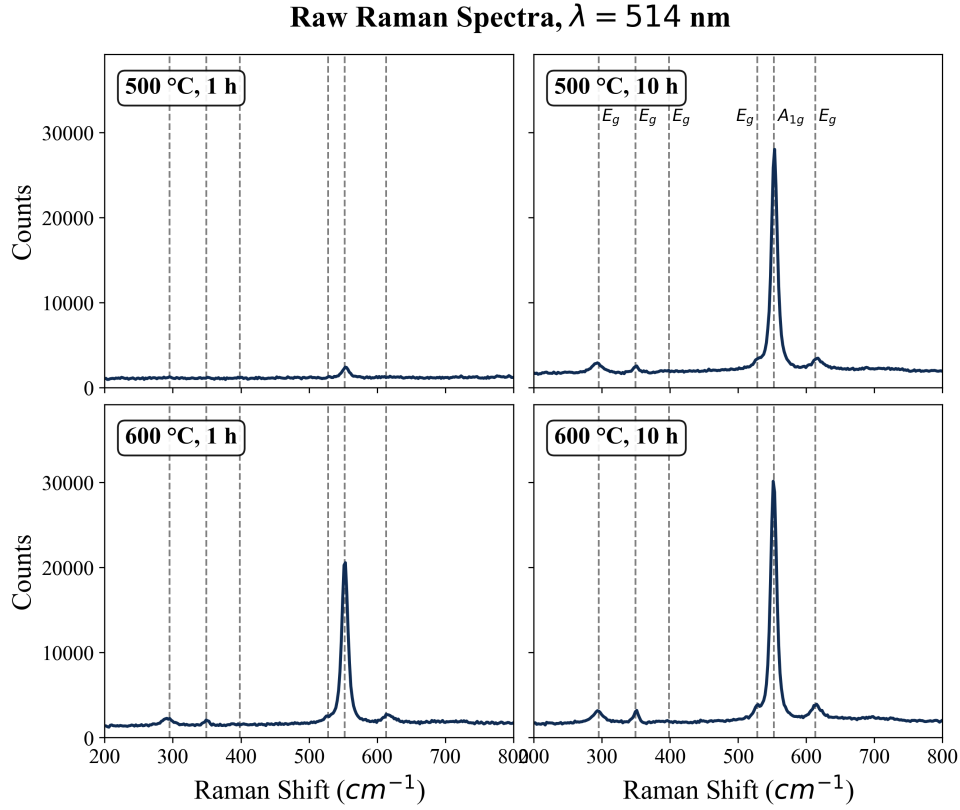


Figure 8.5: Raw Raman spectra ($\lambda = 514$ nm) of the thermally grown chromia scales. The kinetic evolution of the oxide is visually demonstrated from the initial nucleation stage at 500 °C for 1 h (top left) to the mature, highly crystalline scale at 600 °C for 10 h (bottom right).

the formed oxide already possesses periodic long-range crystallographic order. The reason causing the spectra to be so noisy mostly lies behind the extremely limited thickness of the oxide layer, which with only 30 nm offers a minimal scattering volume resulting in a low number of Raman scattering events.

To overcome these physical limitations and successfully probe the vibrational properties of the thinner oxides, multi-wavelength Raman spectroscopy was performed utilizing two additional excitation sources: 457 nm (blue) and 660 nm (red). The primary objective of this comparative analysis is to exploit potential resonance Raman effects to maximize the absorption of the laser in the oxide scale, and subsequently enhance the scattered signal of the ultra-thin scales.

Figure 8.6 shows the Raman spectra collected utilizing the 457 nm excitation source. In this case, all the characteristic chromia peaks reported in the literature [64] are clearly visible, strongly indicating that the oxide formed at 500 °C after 1 hour is already fully

crystalline. As the annealing temperature and time increase, a slight reduction in the spectral noise can be observed, which is consistent with a progressive improvement in the overall crystalline quality. Alongside this, a comparison with the spectra acquired utilizing different excitation wavelengths highlights a distinct variation in the relative intensity ratios of the observed Raman peaks, an effect that is thoroughly examined in Section 8.2.1. Furthermore, another distinctive characteristic of the 457 nm spectra is the appearance of the peak near 398 cm^{-1} , a feature that is completely missing under 514 nm and 660 nm excitation.

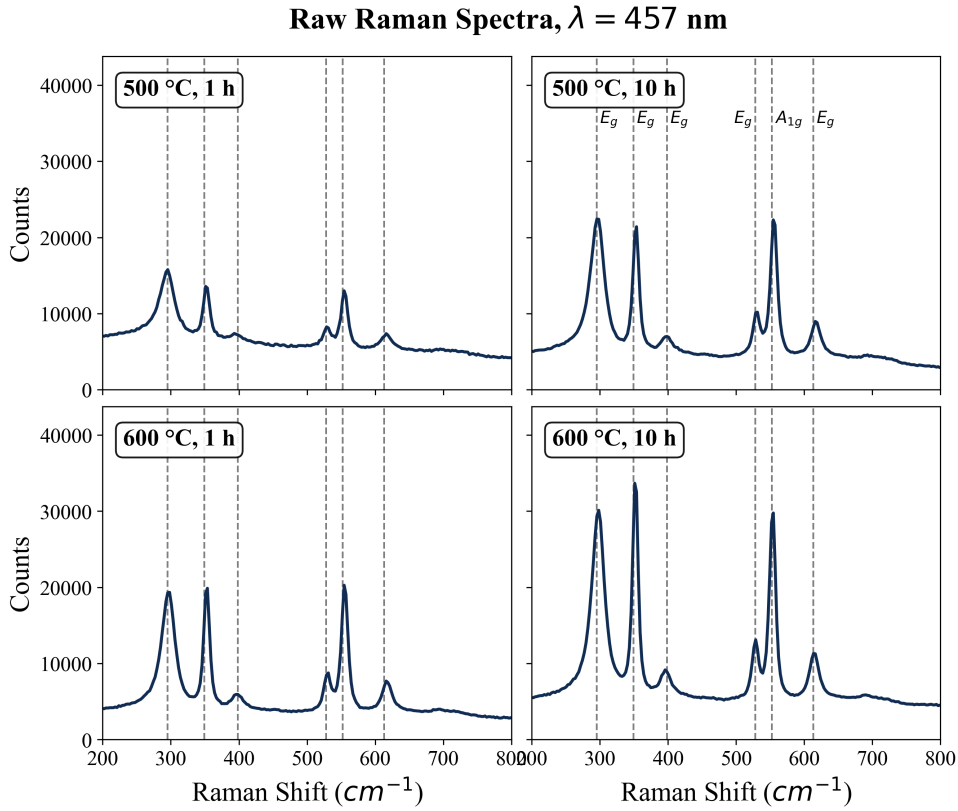


Figure 8.6: Raw Raman spectra ($\lambda = 457\text{ nm}$) of the thermally grown chromia scales. The kinetic evolution of the oxide is visually demonstrated from the initial nucleation stage at 500 °C for 1 h (top left) to the mature, highly crystalline scale at 600 °C for 10 h (bottom right).

Finally the samples were analyzed using the 660 nm excitation source and the results are reported in Figure 8.7. In this case the collected spectra exhibit the worst quality compared to the ones collected with green and blue excitation lines: the noise is higher in all cases and the signal from the thin 500 °C, 1 h oxide does not show any Raman peak at all.

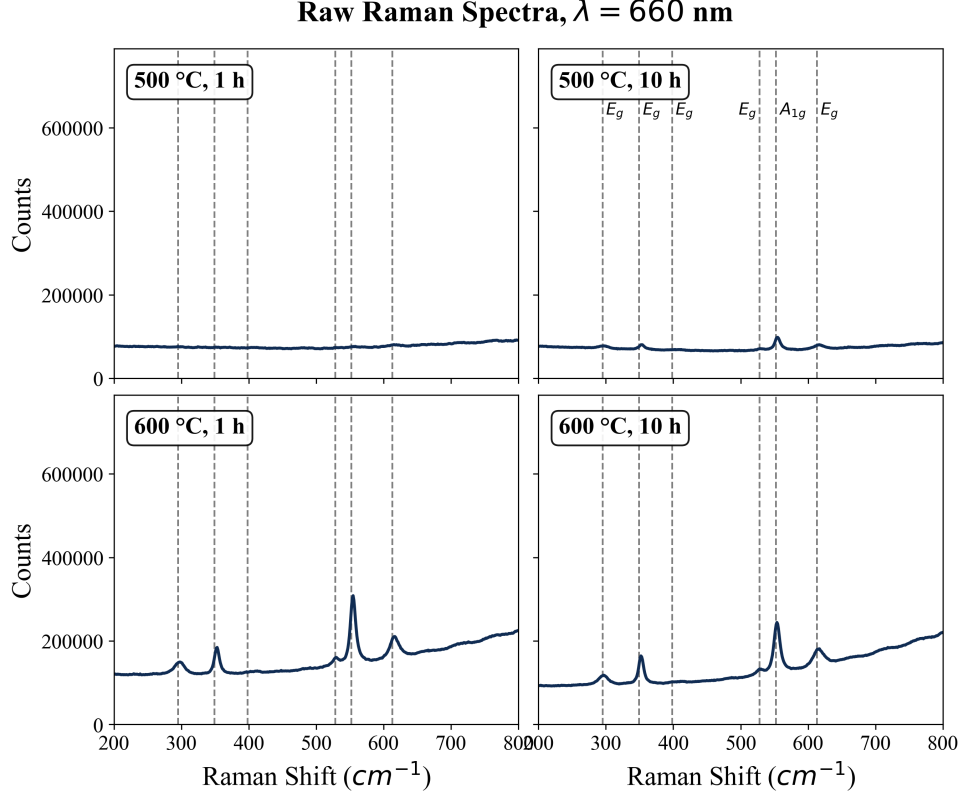


Figure 8.7: Raw Raman spectra ($\lambda = 660$ nm) of the thermally grown chromia scales. The kinetic evolution of the oxide is visually demonstrated from the initial nucleation stage at 500 °C for 1 h (top left) to the mature, highly crystalline scale at 600 °C for 10 h (bottom right).

8.2.1. Analysis of Resonance

The analysis of the spectra reported in the previous section highlights distinct wavelength-dependent behaviors that have not been previously documented in the literature for thermally grown Cr_2O_3 scales. This phenomenon can be explained by considering the optical properties of chromia detailed in Section 4.1.3.

The significant signal enhancement observed in the spectra produced with the 457 nm excitation line can be ascribed to the occurrence of resonant Raman scattering. The incident photons from this blue (2.71 eV) laser match almost perfectly the specific electronic transition denoted as $^4A_{2g} \rightarrow ^4T_{1g}$, previously illustrated in Figure 4.5. According to theory, when the excitation energy corresponds to a real electronic transition within the material, the scattering probability undergoes a massive resonance enhancement, amplifying the Raman signal intensity by up to 10^6 times [108]. As a result, the signal generated by the ultra-thin scale (annealed at 500 °C for 1 h) becomes sufficiently intense to yield

a well-defined spectrum, allowing for the clear identification of the chromia vibrational fingerprint. Furthermore, the standard Raman scattering cross-section is inversely proportional to the fourth power of the excitation wavelength ($1/\lambda_{laser}^4$). This means that the intrinsic intensity of the signal generated by the blue laser is enhanced a priori, even in the absence of resonant phenomena.

It is reasonable to hypothesize that this fundamental $1/\lambda_{laser}^4$ dependence could explain the absence of visible Raman peaks in the spectrum of the same sample when recorded with the 660 nm excitation line. At this longer wavelength, the scattering efficiency drops significantly. It is reasonable that this, coupled with the extremely small interaction volume provided by the ultra-thin oxide, results in a Raman signal completely obscured by the background noise.

Furthermore, the occurrence of resonant Raman scattering is corroborated by the spectral feature already noticed in Section 8.2: the relative intensity of the vibrational modes depends strongly on the excitation wavelength. Specifically, the intensity ratios between the E_g modes primarily associated with chromium sublattice vibrations (centered at 295 cm^{-1} and 352 cm^{-1}) and the principal A_{1g} peak are significantly enhanced under 457 nm excitation compared to the non-resonant 514 nm line. This selective amplification can be directly attributed to the physical nature of the resonance. Because the blue laser photons couple tightly with the spin-allowed intra-band d-d electronic transition involving the highly localized 3d electrons of the Cr^{3+} ions, the vibrational modes dominated by chromium motion experience a much stronger resonance enhancement than those governed primarily by oxygen displacements.

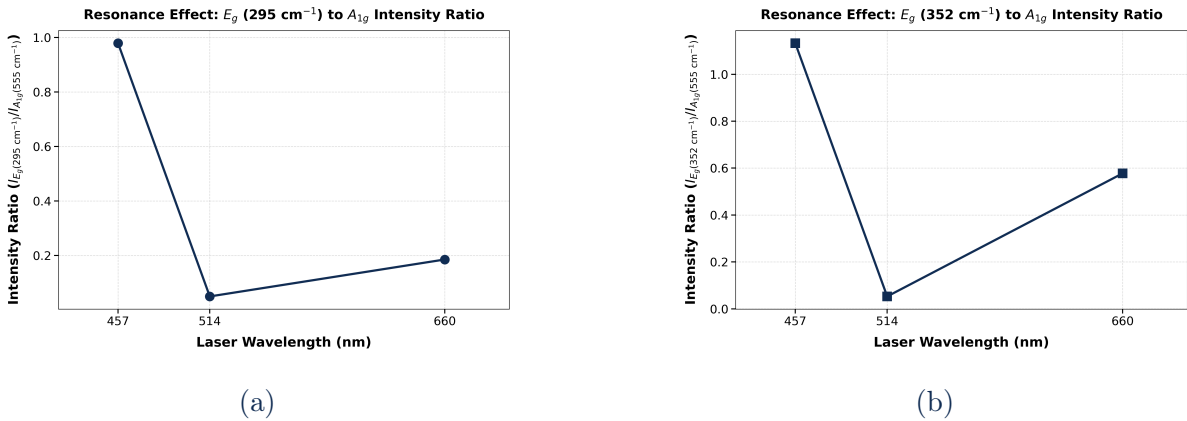


Figure 8.8: Intensity ratios of the E_g to A_{1g} Raman modes as a function of the excitation laser wavelength (457, 514, and 660 nm). Data was extracted from the spectrum of the chromium film annealed at 600 °C for 10 h to demonstrate the selective peak enhancement induced by resonance Raman scattering.

Interestingly, the data reveals that the 660 nm excitation line also induces an increase in these intensity ratios, even though with weaker intensity than the 457 nm source. This intermediate enhancement can be explained by the energetic proximity of the red laser to the spin-forbidden $^4A_{2g} \rightarrow ^2T_{1g}$ transition located at 680 nm. Although this specific electronic transition is inherently weak, the near-resonance condition is still sufficient to trigger a mild, selective amplification of the chromium-dominated E_g modes. Figure 8.8 reports this quantitative trend, explicitly demonstrating the wavelength-dependent selective amplification of the E_g modes (centered at 295 cm^{-1} and 352 cm^{-1}) and visually confirming the described resonant and near-resonant interactions.

To conclude, Figure 8.9 provides a direct visual comparison of the three spectra acquired on the mature oxide scale (600°C , 10 h). This side-by-side juxtaposition clearly illustrates the strong dependence of the Raman signal's quality and intensity on the chosen excitation wavelength.

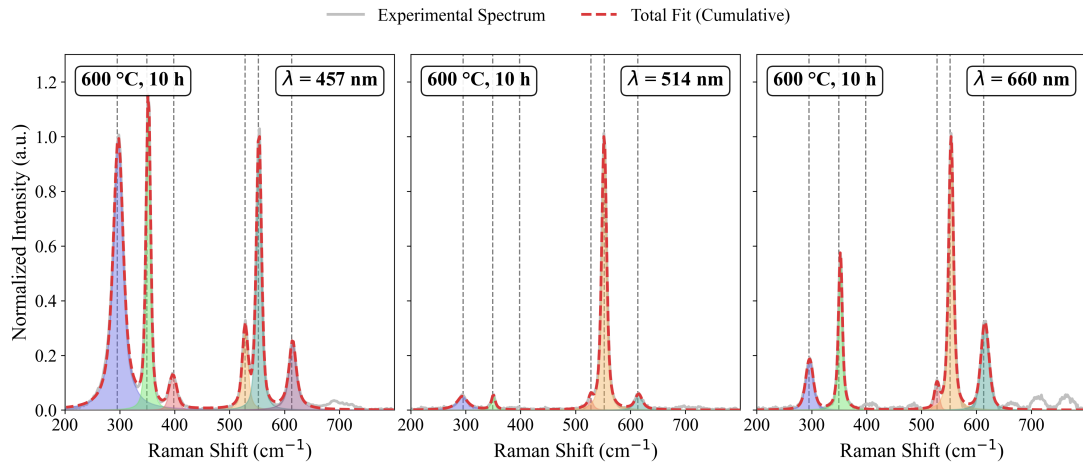


Figure 8.9: Deconvolution of the Raman spectra acquired on the Cr_2O_3 scale grown at 600°C for 10 h, comparing the signal obtained with 457 nm (left), 514 nm (center), and 660 nm (right) excitation wavelengths.

8.2.2. Residual Stress State Evaluation

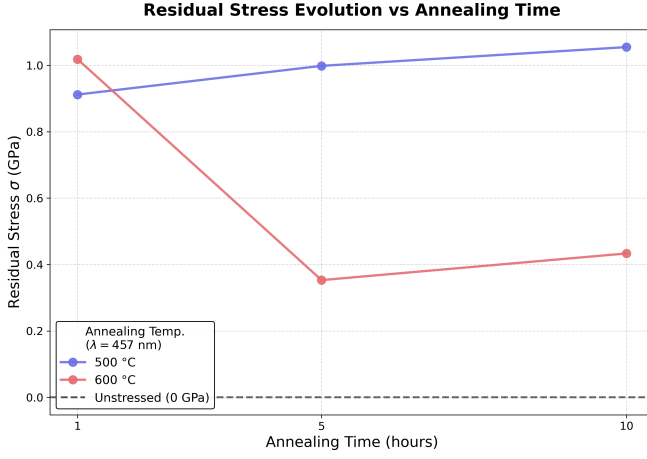
In addition to phase identification, Raman spectroscopy was employed to evaluate the macroscopic residual stresses developed within the thermally grown oxide layers. As detailed in Section 6.2.1, the quantitative stress state of a sample can be directly extrapolated by measuring the shift of a Raman peak relative to its stress-free reference position.

This analysis relies on the principal A_{1g} mode, comparing its measured center position (ν_c) to the stress-free bulk reference (ν_L) reported in Figure 4.2b. Following the methodology

8| Characterization of Chromia Scales Thermally Grown on HiPIMS-Deposited Chromium Films

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established by Mougin et al. [60] and using the Equation 4.2 it was possible to quantify the stress state of the oxide scale. To ensure maximum accuracy, the spectra acquired with the 457 nm excitation line were utilized due to their superior signal-to-noise ratio and well-resolved peak profiles. The calculated stress values are summarized in Table 8.2 and plotted in Figure 8.10, confirming that all the analyzed chromia scales are subjected to macroscopic compressive stress.



Temp. (°C)	Time (h)	σ (GPa)
500	1	-0.912
500	5	-0.998
500	10	-1.055
600	1	-1.018
600	5	-0.353
600	10	-0.433

Table 8.2: Calculated residual stresses.

Figure 8.10: Isothermal evolution of the macroscopic residual stresses within the chromia scale under 457 nm excitation.

According to the literature [49, 74, 64, 109], the buildup of compressive stress in thermally grown chromia films is driven by several physical phenomena. Primarily, growth stresses are generated because the volume of the formed Cr_2O_3 is significantly larger than the volume of the consumed chromium metal, as described by the Pilling-Bedworth ratio higher than 1 [47]. As the oxide grows, it attempts to expand laterally but is restricted by its strong adherence to the rigid metallic substrate, leading to the onset of lateral compressive stresses. Secondly, as the annealing time and temperature increase, stress relaxation mechanisms, such as thermal creep, can be triggered. The efficiency of creep deformation is inversely proportional to the grain size, as grain boundaries facilitate the sliding and diffusion processes necessary for stress accommodation. Consequently, mature, large-grained oxide scales require harsher thermal conditions to activate creep. Finally, thermal stresses are superimposed during the cooling phase from the annealing temperature down to room temperature. Because metallic chromium possesses a higher coefficient of thermal expansion than chromia, the substrate contracts more than the oxide during cooling, generating additional compressive stress in the oxide scale.

The isothermal kinetic evolution of the macroscopic stress at 500 °C and 600 °C is illus-

trated in Figure 8.10. At 500 °C, a weak progressive increase in the compressive stress magnitude is observed over time. In this low-temperature regime, the continuous volumetric expansion associated with the oxidation process dominates. The newly formed oxide is constrained by the substrate, leading to a steady accumulation of growth stress that cannot be efficiently dissipated due to insufficient thermal energy for plastic deformation.

Conversely, at 600 °C, a pronounced decrease in the compressive stress occurs between 1 and 5 hours of exposure. This significant drop suggests that creep-assisted stress relaxation becomes significant at 600 °C. At this temperature, the thermal energy is sufficient to overcome the activation barrier for creep, allowing the oxide scale to plastically deform and relax the accumulated growth stresses. This relaxation phenomenon partially offsets the stress-generation mechanisms that dominate at 500 °C. However, for the sample annealed at 600 °C for 10 hours, the compressive stress begins to rise again. This behavior may be associated with microstructural coarsening of the oxide scale, which is expected to reduce the contribution of grain-boundary-mediated creep mechanisms. As a result, the continuous accumulation of growth and thermal cooling stresses can no longer be fully accommodated, leading to a net increase in the final residual stress state.

In conclusion, from Raman analysis, it is confirmed that the thermally grown chromia scales are characterized by compressive stress. However, such stress state, is well sustained by the samples and no signs of buckling, wrinkling or cracking were reported. Huntz et al. [109] explicitly noted that maintaining a compressive state helps protect the brittle oxide from opening cracks that would otherwise rapidly propagate under tension. Moreover, Khojier et al. [52] observed compressive stress state imparts a significant increase in hardness to the thermally grown chromia compared to bulk chromia.

Altogether, these morphological and vibrational findings indicate that the applied thermal annealing treatments successfully produce compact nanocrystalline Cr_2O_3 scales. However, while Raman spectroscopy provides excellent insight into the macroscopic stress and phase composition, a deeper investigation into the microscopic crystalline quality is required to fully characterize the oxide. To further investigate defect-related phenomena within the oxide scales, photoluminescence measurements were performed.

8.3. Photoluminescence Analysis

Figure 8.11 presents the collected photoluminescence (PL) spectra. Each subfigure displays the spectra of samples annealed at a fixed temperature, with individual lines corresponding to different annealing times. To enable a reliable comparison, all spectra were plotted as a function of energy (eV) and normalized to the maximum intensity of the

principal Raman A_{1g} peak.

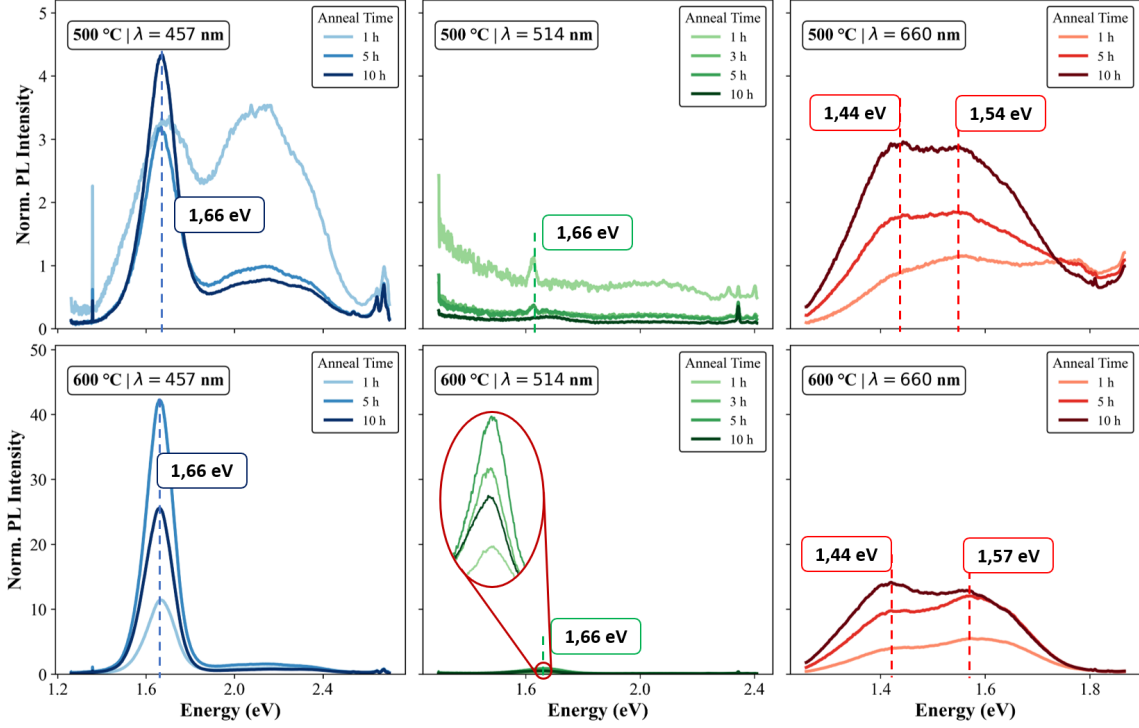


Figure 8.11: Photoluminescence evolution across different excitation wavelengths (457 nm, 514 nm, and 660 nm) for samples annealed at 500 °C and 600 °C. The spectra highlight the dependence of the PL emission on the laser wavelength, with the blue laser exhibiting the most intense bands centered at approximately 1.66 eV. Lower energy bands at 1.44 eV and 1.54–1.57 eV are visible under red laser excitation. All spectra are normalized to the maximum intensity of the main A_{1g} Raman peak.

Because the absolute intensities of both the PL and Raman signals strongly depend on the oxide thickness, this normalization procedure minimizes thickness-related variations, allowing for a more accurate comparison of the PL response.

Analyzing the spectra collected with the 457 nm laser, a prominent emission band is observed at ≈ 1.66 eV. The intensity of this band progressively increases as the oxidation conditions become harsher (longer annealing times and higher temperatures), reaching a maximum in the 600 °C, 5 h condition. However, extending the annealing time to 10 h at 600 °C results in a distinct decrease in PL intensity. The sharp spike visible at 1.35 eV in the 457 nm excitation spectra is an instrumental artifact caused by the of the Rayleigh-scattered laser light inside the spectrometer. The same 1.66 eV band is detected under green laser excitation, although with significantly lower intensity. This stark contrast between the blue and green excitation responses is directly ascribable to the resonance

effect described in previous sections: the material strongly absorbs the blue laser, thereby enhancing the resulting PL emission. Furthermore, red laser excitation enables the identification of two distinct, broad PL bands located at lower energies, specifically centered around 1.44 eV and 1.57 eV.

To the best of the author's knowledge, the specific photoluminescence signature of thermally grown chromia scales remains largely unexplored in the current literature; thus, a tentative physical interpretation is proposed.

The primary emission band centered at 1.66 eV, observed under both blue and green excitation, may be associated with defect-related states caused by point defects within the growing chromia lattice, such as oxygen vacancies or chromium interstitials. These defects alter the local crystal field symmetry, which can drastically enhance the radiative recombination probabilities. Consequently, the increasing PL signal under harsher annealing conditions is consistent with changes in the defect structure. A possible explanation for the subsequent decrease in intensity observed in the 600 °C-10 h sample can be linked to the morphological interpretation provided in Section 8.1. It is hypothesized that, as the crystalline quality of the developing scale improves, vacancies may tend to coalesce at the chromium/chromia interface. Such a structural healing mechanism would reduce the concentration of isolated point defects dispersed within the bulk crystal, explaining the quenched PL intensity in the mature 600 °C-10 h scale.

Additionally, the two broad bands detected exclusively under red excitation suggests the possible existence of other deep defective trap states within the material's band gap.

Given the limited literature available on this specific topic, this photoluminescence analysis provides preliminary insights into the defect-related optical response of thermally-grown chromia scales. Crucially, it highlights the inherently defective nature of the oxide grown via thermal annealing. These initial findings establish a useful baseline that should be further corroborated using complementary defect-sensitive techniques to fully elucidate the complex nature of this luminescent phenomenon.

8.4. Summary of the Oxide Scale Characteristics

The comprehensive morphological, vibrational, and electronic characterizations presented in this chapter contributes to a better understanding of the properties of the thermally grown chromia scales developed on HiPIMS-deposited chromium thin films. By investigating the evolution of the oxide under varying thermal treatments, several fundamental properties of the material have been elucidated. The key experimental findings are syn-

thesized below:

- **Morphology and Growth Kinetics:** Scanning electron microscopy confirmed the growth of continuous, homogeneous, and dense Cr_2O_3 scales across all tested conditions (500 °C to 600 °C for 1 h to 10 h). The microstructure is characterized by equiaxed grains that coarsen with thermal exposure, growing from ≈ 40 nm in the 500 °C, 1 h condition to ≈ 95 nm after 10 h at 600 °C. The thickness of the oxide scales increases with both temperature and time, progressively tending toward an asymptotic value. The thickest oxide layer, grown at 600 °C for 10 h, exhibited an average thickness of 125 nm.
- **Adhesion and Interface Integrity:** All chromium coatings remained firmly adherent to the substrate, exhibiting no signs of wrinkling or macroscopic detachment. Concurrently, the thermally grown oxide layers demonstrated excellent adhesion to the underlying metallic chromium film.
- **Vacancy Coalescence:** In the harshest annealing condition (600 °C for 10 h), localized nanocavities were observed exclusively at the oxide-chromium interface. Their limited dimensions do not compromise the barrier integrity, as they do not create open channels to the external surface. The formation of these interfacial voids is attributed to the thermally driven migration and agglomeration of vacancies, consistent with a possible healing mechanism within the bulk oxide lattice.
- **Phase Purity and Crystalline Quality:** Raman spectroscopy unambiguously confirmed the formation of pure, corundum-phase Cr_2O_3 across all regimes. The high crystalline quality of the mature scales was further corroborated by a strong resonant Raman interaction under 457 nm excitation, uniquely associated with the specific $d - d$ electronic transitions of Cr^{3+} ions in octahedral coordination.
- **Residual Stress State:** All evaluated configurations retained intrinsic compressive residual stress, ranging from 0.353 GPa to 1.055 GPa. This compressive state is highly advantageous from a mechanical perspective, as it inherently counteracts crack propagation and enhances the overall fracture toughness of the ceramic scale.
- **Defect Chemistry and Electronic Structure:** Photoluminescence (PL) analysis revealed defect-related luminescent states, potentially associated with point defects in the chromia lattice. The PL intensity of the band centered at 1.66 eV, which may provide qualitative information on the evolution of defect-related luminescent centers, was observed to peak at the 600 °C-5 h condition. The subsequent decrease in PL signal at 10 h is consistent with the proposed defect-healing mechanism.

In conclusion, the thermal oxidation of HiPIMS-deposited chromium yields a highly compact, fine-grained, and compressively stressed chromia scale. While prolonged high-temperature annealing promotes crystalline maturity and healing of bulk point defects, it simultaneously drives the formation of localized interfacial nanocavities. This fundamental understanding of the microstructural, thermodynamic, and electronic evolution of the oxide scale establishes the necessary scientific foundation for the subsequent phase of this research.

In the following chapter, these properties will be compared to the functional requirements of anticorrosive barriers for Lead-cooled Fast Reactors (LFRs) in order to select the optimal coating configurations and interpret their protective performance during prolonged exposure to highly corrosive liquid lead.

9 | Corrosion Performance of Chromium-Based Bilayer Coatings in Liquid Lead

Building upon the characterization of the thermally grown chromia scales presented in Chapter 8, this chapter presents the results of the corrosion tests conducted on the chromium-based bilayer coatings at the ENEA Brasimone Research Center.

The chapter begins by establishing the rigorous rationale that drove the selection of the two final candidate coatings, highlighting the functional requirements of an ideal anticorrosive barrier. Following a description of the sample preparation and experimental procedure, the core of the chapter provides a post-exposure characterization of the coatings. Through the combined use of Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDXS), and Raman spectroscopy, the degradation mechanisms and microstructural evolution of each configuration are reconstructed. Finally, the chapter concludes with a comprehensive comparative evaluation. By comparing the performance of the two tested coatings against the severe degradation observed on a the bare steel baseline, a possible physical interpretation of the degradation phenomena is provided.

9.1. Rationale for the Selection of Candidate Coatings

By comparing the properties of the oxide scales produced through the various thermal treatments, a rational selection framework is established. This screening allows for the identification of the most promising candidate films to be advanced to a 1000 h exposure campaign within an LFR-relevant liquid lead pool. To provide a rigorous foundation for this selection, the following section synthesizes the key characteristics required for a resilient protective barrier.

Functional Requirements for LFR Protective Barriers

As discussed in Chapter 3, which detailed the fundamental mechanisms of liquid metal corrosion, protective coatings represent the most feasible mitigation strategy for short-term utilization. Based on the specific degradation mechanisms that structural materials must withstand in a liquid lead environment, an efficient anticorrosive barrier must exhibit the following properties:

- **High Morphological Density:** The coating must be fully compact and free of porosity to effectively hinder the macroscopic penetration of the liquid coolant.
- **Atomic-Scale Diffusion Barrier:** A successful anticorrosive film must act as an effective barrier at the atomic scale to block the interdiffusion phenomena of both steel alloying elements and liquid lead. Consequently, possessing low diffusion coefficients for liquid lead and steel alloying elements is a strict requirement.
- **Minimal Surface Roughness:** Surface of an anticorrosive barrier must be as smooth as possible, as minimal roughness minimizes wettability and limits fluid-dynamic interference with the flowing coolant.
- **Self-healing Capability:** Given the harsh operational conditions that coatings must withstand, the ability to automatically heal localized fractures is highly desirable.
- **Mechanical Strength:** Coating materials characterized by high hardness, wear resistance, and elevated fracture toughness are highly desirable to withstand operational mechanical loads.
- **Thermodynamic Stability and Adherence:** The coating material must remain chemically inert and thermodynamically stable across the entire operational temperature range of the reactor while securely maintaining its adherence to the underlying substrate.
- **Radiation Resistance and Thermomechanical Compatibility:** Materials utilized for coating structural components within LFR cores must exhibit high resistance to radiation damage and must not disrupt the global thermomechanical behavior of the components. Specifically, because ceramic coatings possess low thermal conductivity, they are typically engineered with thicknesses in the sub-micrometric range to avoid thermomechanical compatibility issues and prevent thermal stress-induced delamination.

Comparing the above-mentioned requirements with the properties of the chromia scales

summarized in Section 8.4, it was possible to select the coatings with the best characteristics. The two chosen coatings and the reasons motivating the choice are exposed in the following section.

Selection of Optimal Coating Configurations

From the results of Chapter 8, it is evident that all thermally grown oxide scales demonstrated excellent compatibility with the underlying chromium layer. All chromia layers exhibited exceptional adherence and a fine-grained morphology. This fine-grained structure is highly beneficial, as an increased density of grain boundaries enhances the microplasticity of the scale, thereby reducing the inherent brittleness of the ceramic oxide. Furthermore, every tested annealing condition successfully produced a dense barrier without any macroscopic open porosity.

Given that all samples satisfied the baseline structural requirements, the final selection of the candidate coatings for the 1000 h liquid lead exposure campaign was driven by a critical evaluation of four key parameters: scale thickness, residual stress state, crystalline maturity, and expected thermodynamic stability.

Consequently, the high-temperature processing regime was prioritized, specifically selecting the sample annealed at 600 °C for 5 h and the sample annealed at 600 °C for 10 h. The engineering rationale for this selection is detailed below:

- **Maximum Physical Barrier:** These two configurations exhibit the greatest oxide thicknesses (~ 100 nm and ~ 125 nm, respectively). Maximizing the thickness within the safe sub-micron regime was considered the crucial criterion, as a thicker scale acts as a more robust physical barrier.
- **Stress Relaxation:** Both samples are characterized by a moderate compressive stress state (0.353 GPa and 0.433 GPa, respectively), achieved due to the stress relaxation. This relaxed state provides a crucial advantage: it maintains enough compression to enhance crack resistance without approaching the critical yield limits that could trigger buckling or spallation during prolonged reactor operation.
- **Thermodynamic Stability and Lattice Healing:** Prolonged thermal exposure appears to drive the system toward a more thermodynamically stable state. This evolution is consistent with the improved signal-to-noise ratio in the Raman spectra and the reduction of the defect band observed in the photoluminescence analysis at 10 h.

It must be noted that surface roughness showed a tangible increase under these harsher

annealing conditions. While higher roughness could increase the wettability of the coating, this factor was considered secondary; the lower-temperature oxides, though significantly smoother, were too thin to guarantee long-term protection.

Ultimately, the comparison between the 5 h and 10 h configurations at 600 °C provides insight into two competing microstructural phenomena: the 10 h sample exhibits higher crystalline quality but develops nanopores at the oxide-chromium interface, whereas the thinner 5 h oxide does not show such voids but retains a higher photoluminescence signal from defects. In the following, the samples annealed at 600 °C for 10 h will be referred to as Coating-Chromia-10, while the sample annealed for 5 h will be denoted as Coating-Chromia-5.

The two selected coating configurations have been replicated on stainless steel substrate and exposed to reactor-relevant stagnant liquid lead at 600 °C for 1000 h (further details about the testing facility are reported in Section 7.1). The microstructural evolution and the corrosion resistance of these chosen bilayer configurations are extensively analyzed and discussed in the next sections.

9.2. Samples Preparation

To assess the anticorrosive efficacy of the selected coatings, testing samples were synthesized following the identical deposition and thermal annealing protocols detailed in Chapter 8. However, to replicate relevant operational conditions, the idealized silicon substrates were replaced with structural steel. Specifically, the coatings were deposited on AISI 316L austenitic stainless steel, which serves as the standard reference material for the extensive material screening campaign currently ongoing at the ENEA Brasimone research facility.

In detail, 1 μm -thick chromium films were deposited via HiPIMS by a colleague at the NanoLab research team, utilizing the exact deposition parameters outlined in Table 5.1. The morphological characteristics of the samples prior to the corrosion campaign are presented in Figure 9.1. The stainless steel substrates have dimensions of $1 \times 5 \text{ cm}$, featuring a through-hole in the upper region to facilitate secure mounting to the support structure during the liquid lead exposure test.

Figures 9.1a-c confirm the successful deposition of the metallic film onto the structural steel substrates. Both the cross-sectional and planar morphologies are highly consistent with those observed in the analogous chromium films grown on silicon substrates (Chapter 8). However, as illustrated in Figure 9.1d, localized deposition anomalies are occasionally

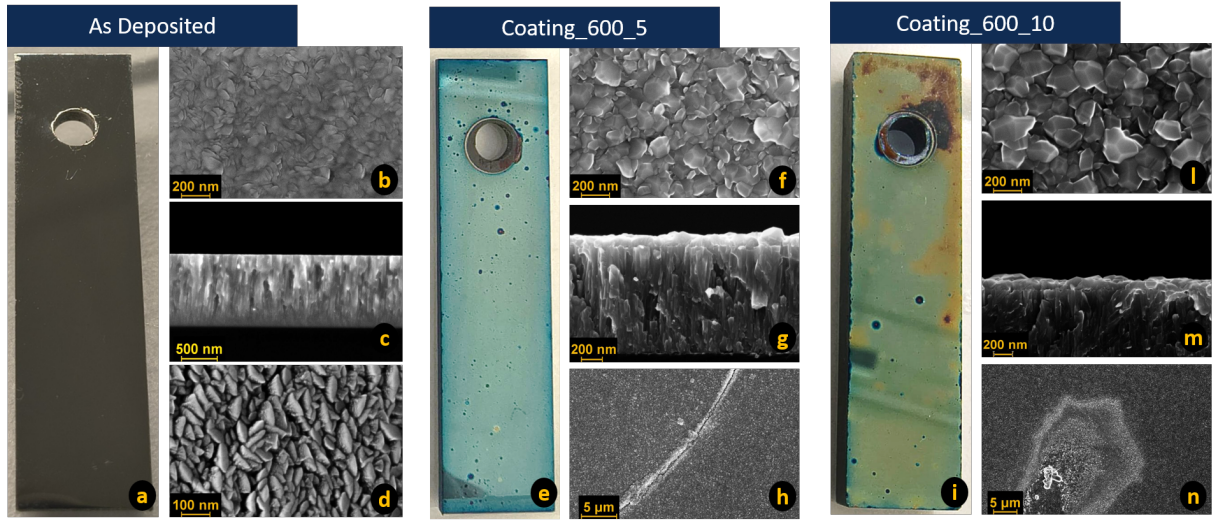


Figure 9.1: Macroscopic and microstructural characterization of the coated AISI 316L substrates prior to liquid lead exposure. The panels correspond to the as-deposited chromium film (a-d), Coating-Chromia-5 annealed for 5 h (e-h) and the Coating-Chromia-10 produced via annealing at 600 °C for 10 h (i-n). For each condition, the images display: (a, e, i) macroscopic visual appearance; (b, f, l) planar grain morphology via top-view SEM; (c, g, m) coating architecture via cross-sectional SEM; and (d, h, n) representative localized surface defects.

present. Due to the inherent irregularities of the commercial steel surface, the macroscopic coating morphology is not perfectly smooth in all regions. These irregularities suggest that the columnar grains locally deviated from a strictly perpendicular growth orientation, generating the irregular micro-texture captured in the planar SEM micrograph.

Figures 9.1e-g and 9.1i-m report the macroscopic appearance and microscopic morphology of the two bilayer chromium-chromia configurations following the thermal annealing treatments. The microstructural features of the thermally grown oxide scales perfectly mirror those achieved on the silicon substrates, aside from isolated microscopic defects (Figures 9.1h and 9.1n). Specifically, Figure 9.1n highlights a localized micro-crater, likely nucleated at an irregularity on the underlying steel substrate, whereas Figure 9.1h reveals a micro-crack within the coating. Nevertheless, these superficial defects are not expected to severely compromise the global structural integrity of the protective barrier; visual and microstructural inspections verify that the thermal oxidation process successfully generated a continuous passivating layer that covers the macroscopic surface and the observed defects.

Furthermore, supplementary Raman spectroscopy characterization confirmed that the

production procedure on structural steel yielded chromia scales possessing the identical structural quality as those detailed in Chapter 8.

Experimental Procedure

To evaluate the anticorrosive efficacy of the selected coatings, the following procedure was followed:

1. **Samples Preparation:** Three identical coated specimens were produced for each selected annealing condition (600 °C for 5 h and 600 °C for 10 h): one sample was preserved in its pristine state as a baseline reference, while the remaining two were dedicated to the corrosion tests.
2. **Liquid Lead Exposure:** A total of four coated specimens (two per configuration) were installed in the CAPSULE facility hosted at the ENEA Brasimone Research Center. The samples were immersed in the static liquid lead pool for a duration of 1000 h at an operating temperature of 600 °C. Throughout the experiment, the concentration of dissolved oxygen within the heavy liquid metal was kept at 10^{-7} wt%.
3. **Extraction and Chemical Washing:** Upon completion of the 1000 h exposure, the samples were extracted from the facility and allowed to cool to room temperature, resulting in the natural solidification of residual lead on their surfaces. To facilitate post-exposure analysis, one sample from each coating configuration underwent a chemical washing procedure, as described in Chapter 7.1. The duplicate sample for each configuration was left unwashed. This comparative approach was adopted to investigate the potential morphological and chemical alterations induced by the washing procedure itself, thereby isolating its effects from the actual corrosion phenomena.
4. **Mechanical Sectioning and Encapsulation:** To enable cross-sectional evaluation, a portion of each exposed sample was mechanically sectioned and embedded in a polymeric resin matrix. It must be explicitly noted that all post-exposure sample handling operations, including the chemical washing, mechanical sectioning, and resin encapsulation, were performed entirely on-site at the ENEA Brasimone facility.
5. **Microstructural Characterization:** The prepared cross-sections and planar surfaces were subsequently transferred to the NanoLab facilities at Politecnico di Milano. Here, a comprehensive post-corrosion characterization was conducted utiliz-

ing Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDXS), and Raman spectroscopy.

Through this multimodal analysis, the protective behavior of the coatings and the specific microstructural modifications induced by the heavy liquid metal environment were assessed. The subsequent sections present these findings in detail. First, macroscopic visual inspection was utilized to identify global morphological changes and evaluate the physical impact of the chemical cleaning procedure. Subsequently, scanning electron microscopy (SEM) was employed to characterize the microscopic signs of coating-lead interaction on both the planar surfaces and the cross-sections. This was coupled with EDXS analysis to track elemental redistribution and potential dissolution profiles. Finally, Raman spectroscopy was used for precise structural identification of the different phases that developed due to the high-temperature interaction with liquid lead.

Following the individual characterization of the samples, a comparison between the performances of the two coating configurations is provided, along with a physical interpretation of the observed phenomena. To validate the enhancement in corrosion resistance provided by the engineered barriers, the uncoated rear surface of the substrates was analyzed as a baseline reference. It must be specified that while this surface lacked the HiPIMS chromium layer, it underwent the identical thermal annealing treatments, leading to the growth of an oxide scale. Although this pre-oxidation likely provided a barrier effect, evaluating this native scale proved fundamental to validating the severe corrosivity of the environment.

9.3. Corrosion Performance of Coating-Chromia-5

Planar Morphology and Surface Analysis

Figures 9.2a and 9.2b display the macroscopic appearance of the unwashed and chemically cleaned Coating-Chromia-5 samples, respectively. Visual inspection of the unwashed sample reveals that solidified lead adhered to the entirety of the exposed surface. Conversely, the chemically cleaned sample reveals a surface that has been completely altered by the exposure to liquid lead. Compared to its pristine state (Figure 9.1e), the exposed surface has lost its original reflectivity and exhibits a completely non-metallic, opaque appearance.

To investigate potential morphological artifacts introduced by the chemical cleaning procedure, a scale of solidified lead was mechanically removed from the unwashed sample. Figures 9.2D1 and 9.2D2 present the SEM images of the surface exposed beneath this

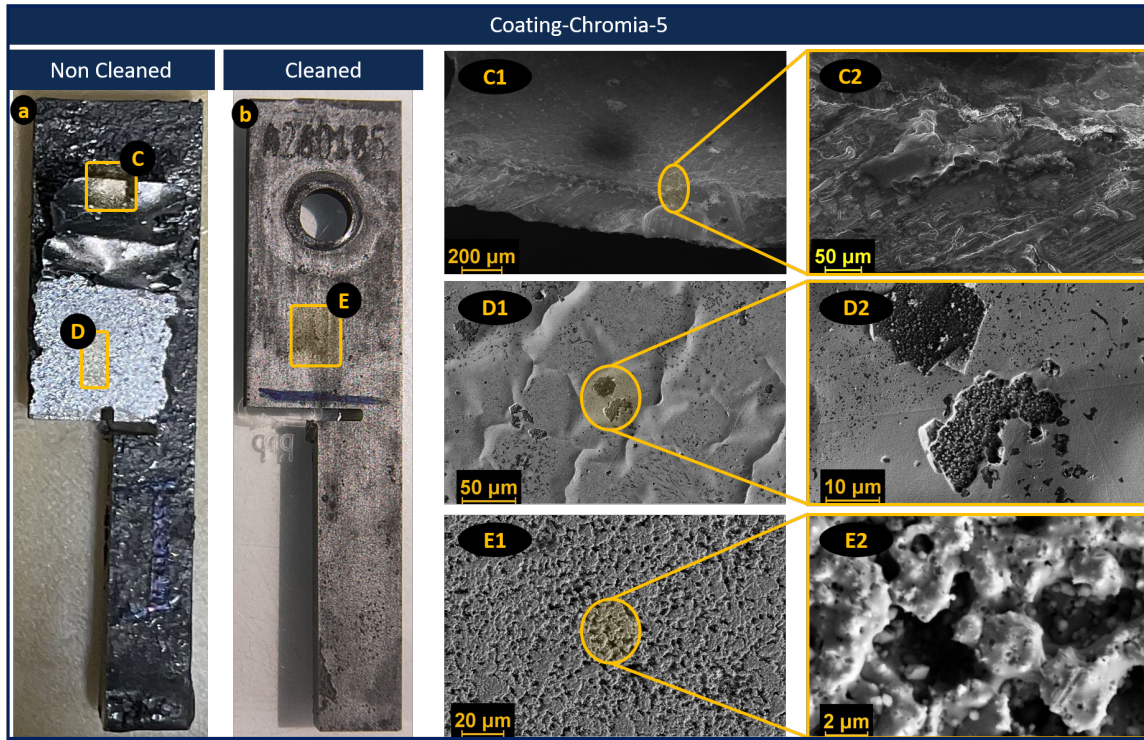


Figure 9.2: Post-corrosion morphological characterization of Coating-Chromia-5h. (a, b) Macroscopic appearance of the non-cleaned and cleaned samples, respectively. SEM micrographs detail: (C) cross-sectional view of a mechanically removed solidified lead; (D) planar surface morphology beneath the removed lead; and (E) superficial morphology of the chemically cleaned sample.

removed lead layer. This area also appears heavily modified by the corrosion test, differing significantly from the characteristic morphology of the pristine oxide scale (Figure 9.1f). Figures 9.2C1 and 9.2C2 display the cross-sectional SEM images of the mechanically removed lead flake. This specific analysis was conducted to verify whether the protective coating had delaminated and remained attached to the lead during the mechanical removal. No traces of the coating were detected within the removed lead scale.

Furthermore, Figures 9.2E1 and 9.2E2 show the SEM micrographs of the chemically cleaned sample's surface at varying magnifications. The microscopic view provides further evidence that the original surface topography was completely degraded by the high-temperature interaction with the liquid lead.

Figure 9.3 shows the planar EDXS elemental maps of the chemically cleaned Coating-Chromia-5 sample. The elemental composition of the surface is highly inhomogeneous. Across the majority of the mapped area, strong signals from oxygen and the constitutive elements of the steel substrate (Fe, Cr, Mn, Ni) are prevalent. However, several localized

regions exhibit a complete absence of these substrate elements, revealing exclusively the signal of Pb.

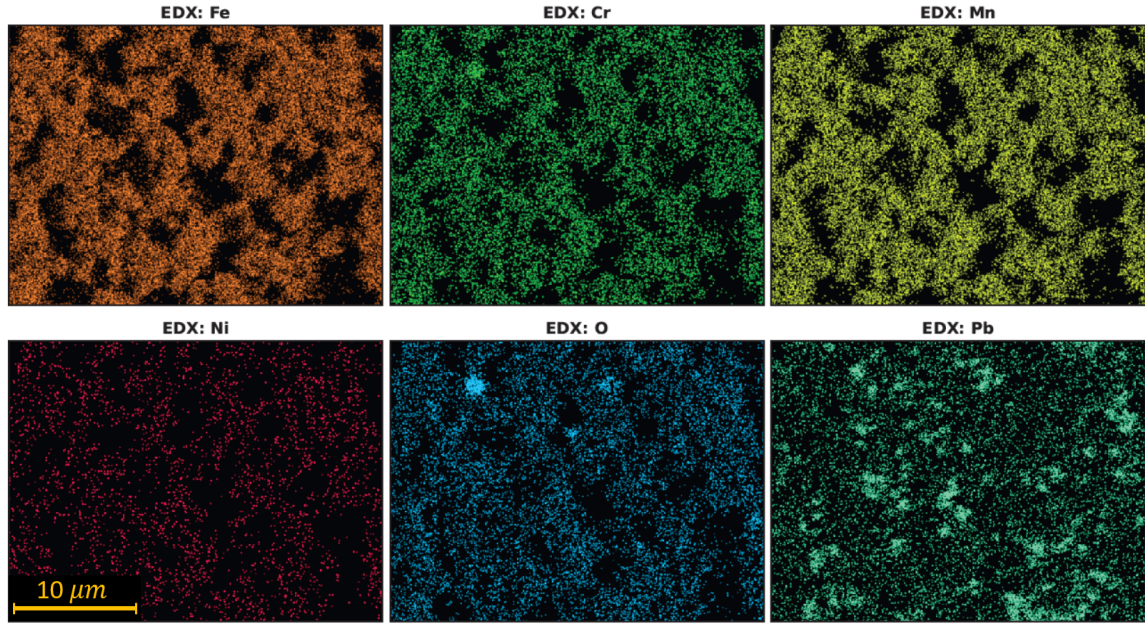


Figure 9.3: Planar EDXS elemental mapping of the chemically cleaned Coating-Chromia-5 sample. The mapped region corresponds to the surface morphology shown in Figure 9.2E.

These distinct, Pb-rich islands suggest a severe, localized failure of the protective chromia scale, where heavy liquid metal penetrated the underlying steel, driving a localized dissolution attack (pitting). As the liquid lead dissolved the substrate, it created microscopic craters. Upon cooling, the lead solidified and remained embedded in the substrate and was not removed by the superficial chemical cleaning procedure.

To gain deeper insights into the structural state of the sample and to identify the nature of these surface alterations, Raman spectroscopy was utilized to characterize the phases present across the different regions of the samples. The 457 nm (blue) excitation wavelength was used because of the capability described in Chapter 8 to enhance the signal associated with chromia. Reference spectra utilized for the identification of these characteristic vibrational fingerprints are provided in [110–113].

Figure 9.4a presents the Raman signal acquired from the surface of the chemically cleaned sample. No peaks associated with lead oxides, suggesting that the Pb detected via EDXS mapping was probably not oxidized (pure lead has no Raman signal). The detected prominent peaks correspond to iron oxides and mixed Fe-Cr spinels, which strongly suggests that iron atoms from the AISI 316L substrate outward-diffused through the protective

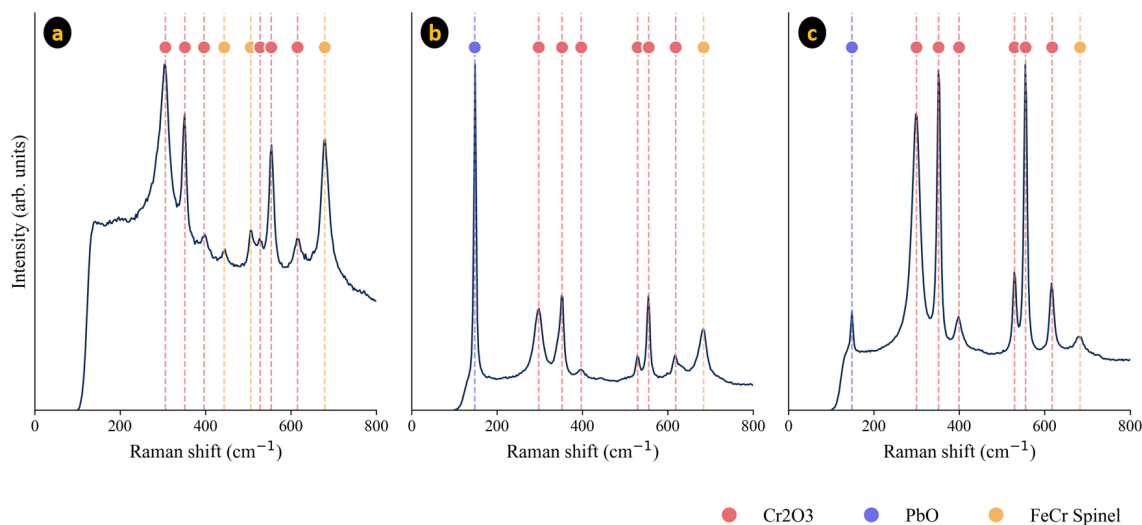


Figure 9.4: Raman spectra acquired from distinct regions of the corroded Coating-Chromia-5 sample. (a) Raman spectrum of the surface of the chemically cleaned sample. (b) Raman spectrum of the inner face of the removed solidified lead flake. As the observed surfaces exhibit microscopic heterogeneity, multiple spectra were acquired for each region; the most representative ones are reported here. (c) Raman spectrum of the sample surface exposed beneath the mechanically removed solidified lead.

barrier and reacted with the dissolved oxygen in the lead pool. Additionally, the characteristic peaks of chromia remain distinguishable, suggesting that at least a portion of the original coating may still be present.

The spectra obtained from the surface beneath the removed lead (Figure 9.4b) and the inner surface of the removed lead flake itself (Figure 9.4c) exhibit high similarity. In both regions, chromia is identified alongside iron oxides and mixed Fe-Cr spinels. Furthermore, the intense and sharp peak associated with PbO is detected.

While these planar data provide clear evidence of an interaction between the underlying steel substrate and the heavy liquid metals, definitive conclusions regarding the overall degradation of the Coating-Chromia-5 barrier cannot be drawn from surface analysis alone. Consequently, a detailed cross-sectional investigation is required to reconstruct the failure mechanisms.

Cross-Sectional Analysis

Cross-sectional morphological analysis proved fundamental for reconstructing the degradation mechanisms and assessing the impact of the cleaning procedure. Figure 9.5a displays the cross-sectional SEM micrograph of the chemically cleaned sample. No trace of

the protective coating is detected; furthermore, the exposed surface of the steel substrate exhibits severe signs of corrosive attack, characterized by localized channels and pits penetrating to a maximum depth of approximately 10 μm . Conversely, Figure 9.5b presents the cross-sectional SEM image of the unwashed sample. In this micrograph, an intermediate layer is clearly visible between the solidified lead and the steel substrate. This provides strong evidence that the original bilayer coating was not completely dissolved during the liquid metal exposure, although its structural integrity appears significantly compromised.

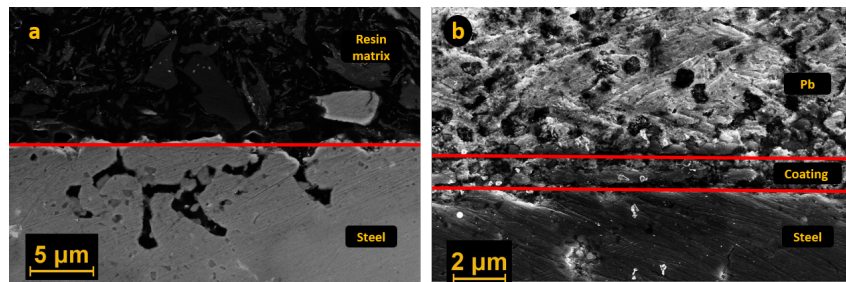


Figure 9.5: Cross-sectional SEM micrographs of the Coating-Chromia-5 sample following the 1000 h liquid lead exposure: (a) chemically cleaned sample; (b) unwashed sample.

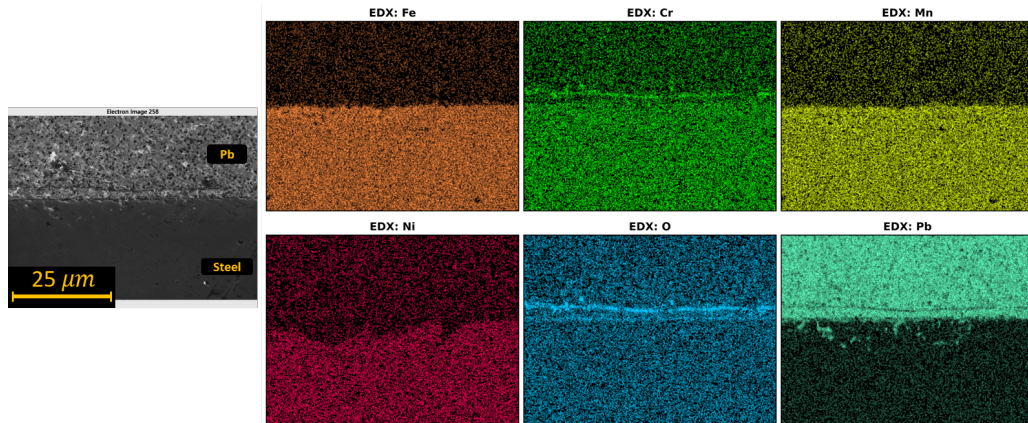


Figure 9.6: Cross-sectional EDXS elemental mapping of the unwashed Coating-Chromia-5 sample, highlighting the severe infiltration of liquid lead (Pb) through the barrier and the resulting sub-surface depletion of nickel (Ni).

The corresponding EDXS elemental maps of the unwashed sample, presented in Figure 9.6, confirm that the substrate surface remains covered by the remnants of the barrier, as evidenced by the accumulation of chromium and oxygen at the interface. However, an analysis of the lead and nickel distributions unambiguously reveals the failure of the protective scale.

The Pb map confirms the severe inward penetration of the liquid coolant through the barrier and into the underlying steel, reaching a maximum depth matching the 10 μm pits observed in the cleaned sample. Within the residual coating region itself, the lead signal is highly intense, highlighting a massive infiltration of the heavy liquid metal. Concurrently, the Ni map reveals a large depletion zone immediately beneath the original chromium-steel interface, which is a definitive signature of severe localized dissolution driven by the liquid lead attack.

Further discussion and interpretation of the corrosion mechanisms occurred to Coating-Chromia-5 sample is given in Section 9.5, together with a comparison with the performance of Coating-Chromia-10 barrier.

9.4. Corrosion Performance of Coating-Chromia-10

Planar Morphology and Surface Analysis

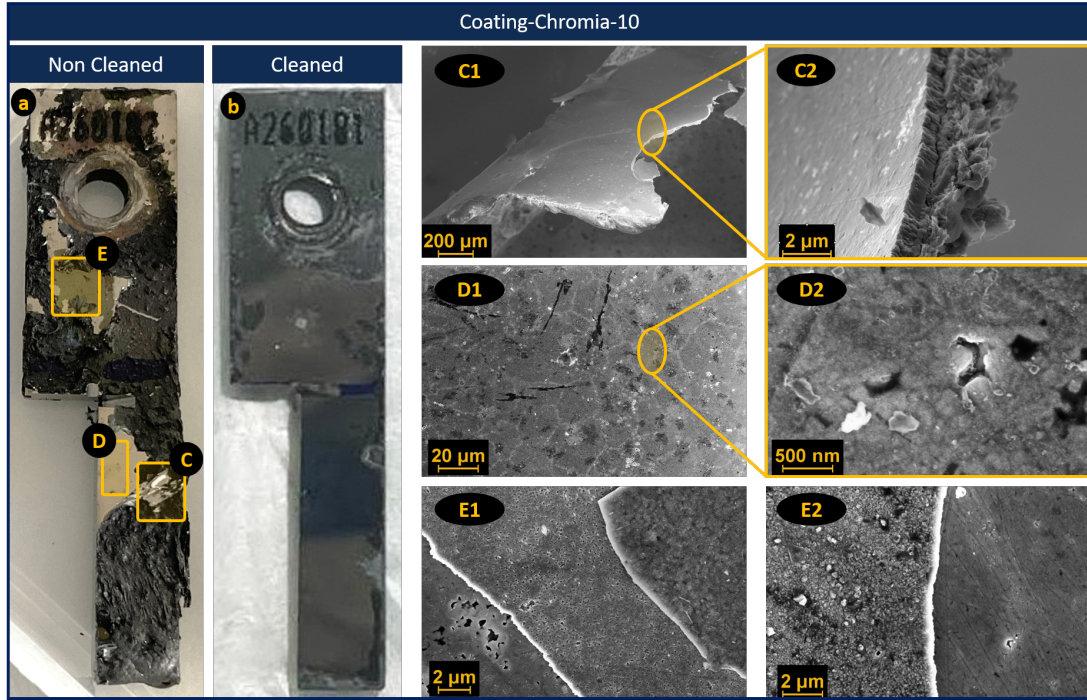


Figure 9.7: Post-corrosion morphological characterization of Coating-Chromia-10. (a, b) Macroscopic appearance of the unwashed and chemically cleaned samples, respectively. (C1, C2) cross-sectional view of the mechanically removed lead flake, with the coating clearly distinguishable; (D1, D2) planar surface morphology beneath the removed lead, which is identical to that of the cleaned sample. (E1, E2) residual coating morphology in regions free from solidified lead.

The post-exposure macroscopic appearance of the Coating-Chromia-10 samples differs drastically from that of the Coating-Chromia-5 configuration. As shown in Figure 9.7b, the chemically cleaned sample exhibits a smooth, highly reflective metallic surface, closely resembling the bare stainless steel substrate. Conversely, visual inspection of the unwashed sample (Figure 9.7a) reveals that the solidified lead strongly adhered to and completely covered the majority of the exposed surface.

However, a specific macroscopic region on the unwashed sample (labeled as Region E) remained free from the heavy liquid metal scale. This area exhibits a complex morphology: while some portions are reflective and metallic, the majority of the surface is opaque with a greenish-yellow appearance, highly reminiscent of the pristine thermally grown oxide

(Figure 9.1i). Representative SEM micrographs of this area (Figures 9.7E1 and 9.7E2) reveal a "triple-layer" architecture ascribable to the initial structure: the underlying steel substrate, the HiPIMS-deposited chromium film, and the external oxide scale.

The planar EDXS mapping (Figure 9.8) corroborates this structural interpretation. In the bottom-left corner, a high concentration of substrate elements confirms the exposure of the bare steel. In the central region, the signal is predominantly chromium, identifying the intermediate HiPIMS layer; however, well-defined polygonal domains within this layer show intense signals of Fe, Ni, and Mn, indicating an outward diffusion of the steel alloying elements.

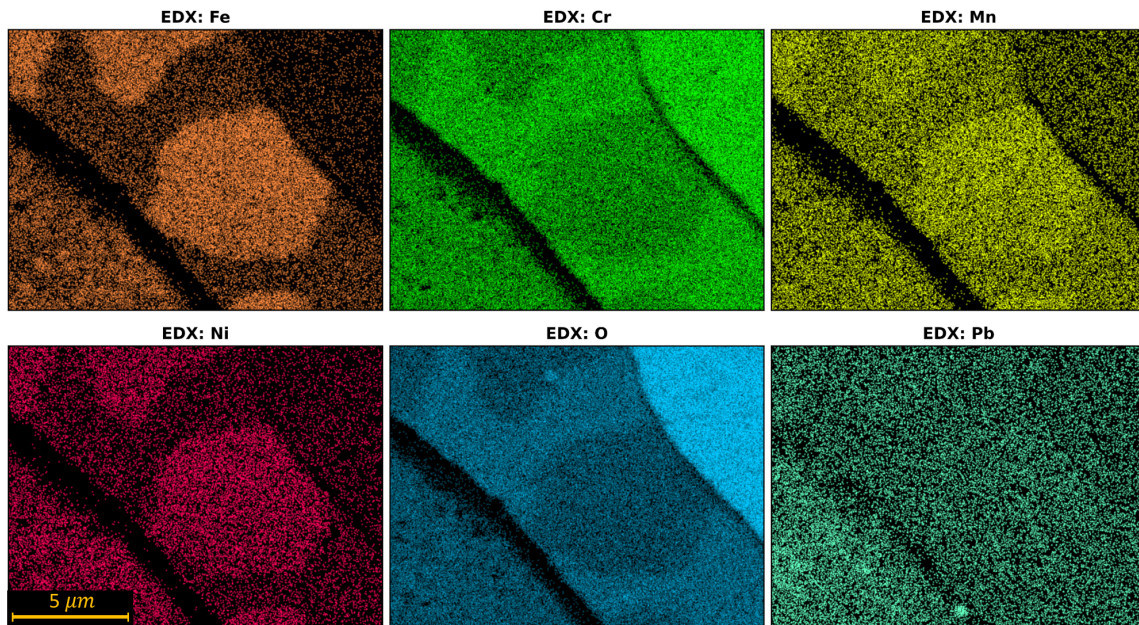


Figure 9.8: Planar EDXS elemental mapping of the unwashed Coating-Chromia-10 sample. The mapped region corresponds to the "triple-layer" surface morphology previously shown in Figure 9.7E1.

Finally, the top-right corner is heavily dominated by chromium and oxygen, suggesting that the external chromia scale successfully preserved its composition in this specific location. The elemental signal of Pb across these regions remains uniform, with no localized accumulations. Nevertheless, high-magnification SEM analysis (Figures 9.7E1 and 9.7E2) reveals the formation of nano-pits and localized micro-craters on both the exposed steel substrate and the intermediate chromium film.

Further structural characterization of this surviving oxide region was conducted via Raman spectroscopy. As illustrated in Figure 9.9, the area is microscopically heterogeneous. The majority of the surface exhibits a lighter optical appearance (Figure 9.9a), and its

Raman spectrum is dominated by the sharp peaks of pure chromia (Cr_2O_3). However, embedded within this chromia matrix are localized darker domains (Figure 9.9b), whose Raman signature corresponds predominantly to mixed Fe-Cr spinels. This further confirms the localized outward diffusion of iron detected by EDXS.

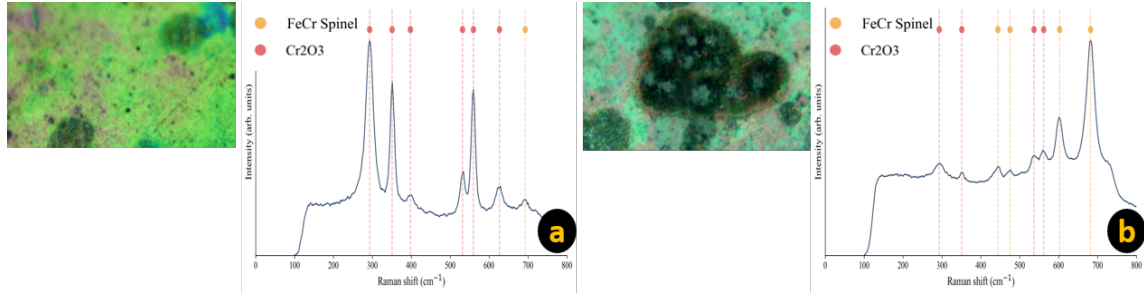


Figure 9.9: Raman spectra acquired from the intact regions of the Coating-Chromia-10 sample (region E in Figure 9.7a), highlighting the heterogeneity of the observed oxide scale.

To investigate the surface condition beneath the adhered heavy liquid metal, the approach of mechanically removing a flake of solidified lead was repeated. Figures 9.7C1 and 9.7C2 detail the interface of this extracted flake at varying magnifications. Figure 9.7C2 demonstrates that the protective coating completely detached from the substrate and remained attached within the solidified lead. The morphology of this detached coating appears similar to its pristine, pre-exposure state.

Finally, Figures 9.7D1 and 9.7D2 present SEM micrographs of Region D, where the bare substrate was exposed following the mechanical removal of the solidified lead scale. These images are also highly representative of the surface morphology of the chemically cleaned Coating-Chromia-10 sample, which exhibited identical features. The SEM analysis confirms the presence of the aforementioned nano-pits, contrasting with the metallic-like reflectivity observed macroscopically on the surface. Notably, these pits appear to be preferentially localized along specific networks, which are attributed to the grain boundary regions of the stainless steel substrate (Figure 9.7D1). Planar EDXS analysis of this exposed substrate surface revealed no detectable presence of Pb where the nano-pits are located, as shown in Figure 9.10.

In summary, the planar morphological and chemical analysis clearly demonstrates that the performance of the Coating-Chromia-10 configuration differs substantially from that of the Coating-Chromia-5 sample. To fully elucidate these structural differences and evaluate the underlying degradation mechanisms, the following section presents the data collected through cross-sectional characterization.

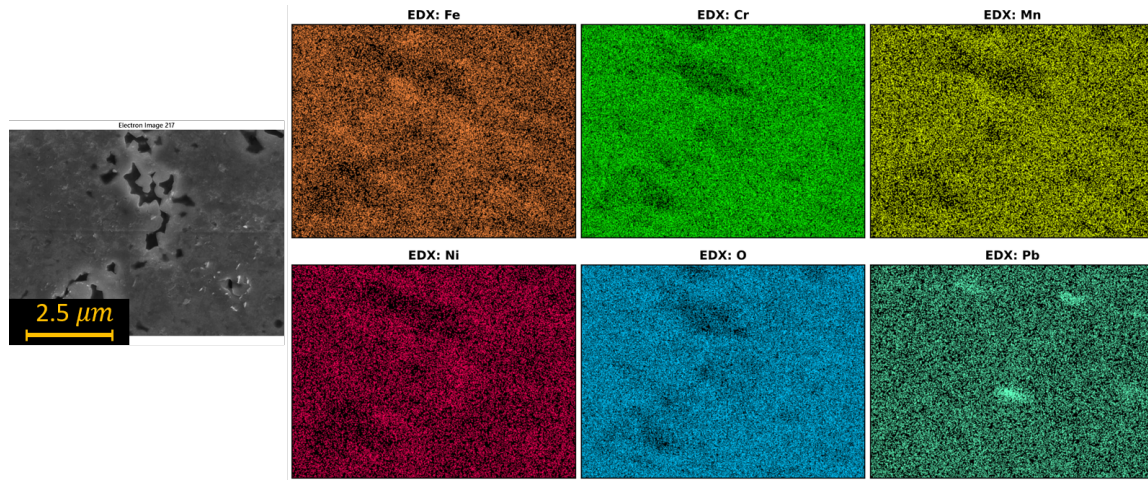


Figure 9.10: Planar EDXS elemental mapping of the substrate surface exposed after the mechanical removal of the solidified lead scale from the unwashed Coating-Chromia-10 sample.

Cross-Sectional Analysis

Regarding the chemically cleaned specimen, Figure 9.11a presents the cross-sectional SEM micrograph of the surface.

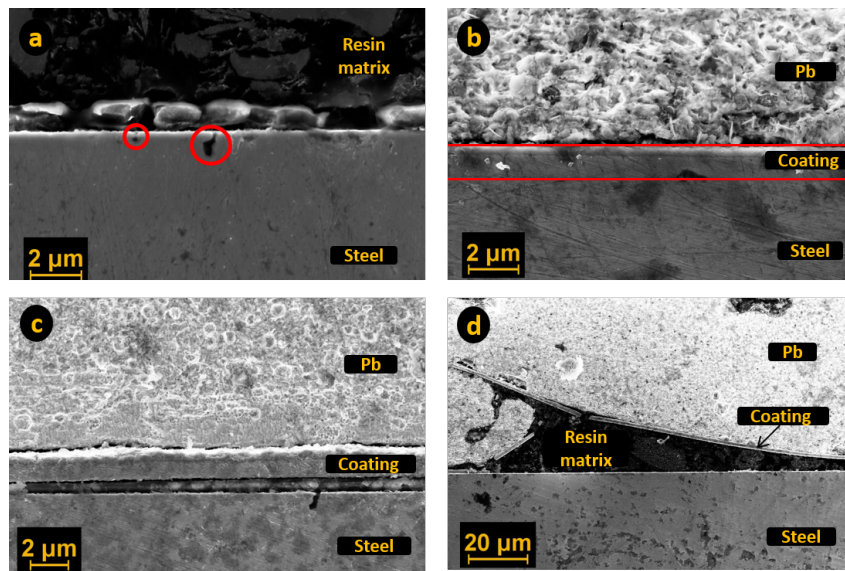


Figure 9.11: (a) Cross-sectional SEM micrograph of the Coating-Chromia-10 chemically cleaned sample after corrosion test. (b, c, d) images of different regions of the cross-sectional view of the unwashed Coating-Chromia-10 sample after corrosion test.

No remnants of the protective coating are detected. Nonetheless, the exposed surface of the steel substrate appears almost unaffected by heavy corrosion mechanisms, showing

only a few superficial nano-defects (circled in red). The fine particulate matter observed at the interface between the resin and the steel substrate consists of contaminants trapped during the post exposure procedures, rather than corrosion products.

Conversely, Figures 9.11b, 9.11c, and 9.11d display cross-sectional SEM micrographs of the unwashed sample. The majority of the unwashed cross-section exhibits the morphology shown in Figure 9.11c: the coating is clearly present and physically separates the solidified lead scale from the underlying steel substrate. The substrate surface itself exhibits excellent integrity, showing only a few isolated nanometric surface defects.

However, the coating has detached from the substrate. Figure 9.11d shows another region where this delamination is even more pronounced. Furthermore, these two micrographs reveal that no trace of liquid lead managed to infiltrate the gap formed between the detached coating and the substrate. This is particularly evident in Figure 9.11d, where the region beneath the delaminated barrier is filled exclusively by the embedding resin, and not by liquid lead. In contrast, Figure 9.11b captures a region of the cross section where the coating successfully maintained its adherence to the steel substrate. In this micrograph, red lines are utilized to delineate the intact interfaces: the lower line marks the substrate-chromium boundary, while the upper line highlights the transition between the metallic chromium film and the external thermally grown oxide scale.

The cross-sectional EDXS elemental maps presented in Figure 9.12 corroborate the preservation of the barrier, confirming the continuity of the intermediate chromium film and the external oxide scale.

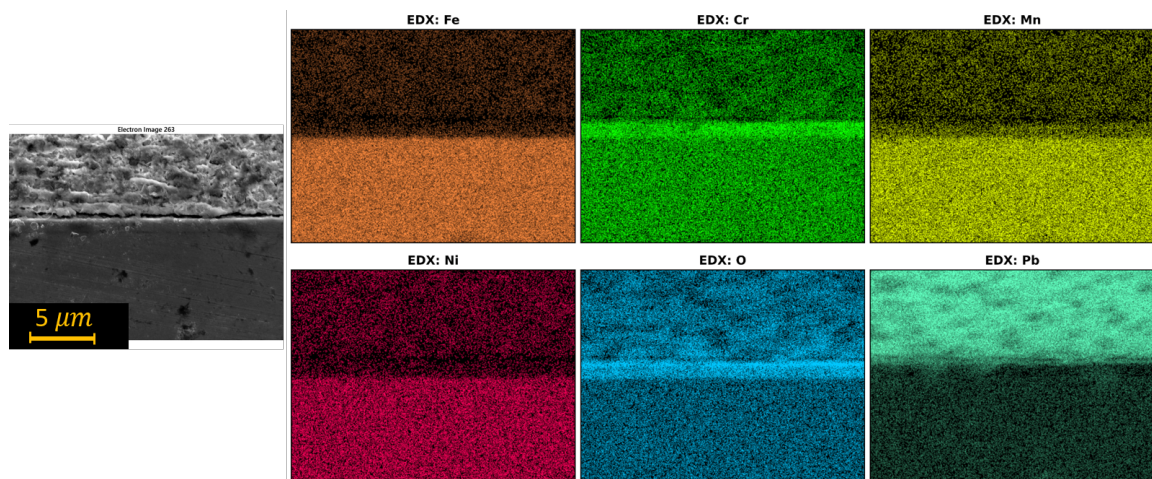


Figure 9.12: Cross-sectional EDXS elemental mapping of the unwashed Coating-Chromia-10 sample, demonstrating the preservation of the chromium/chromia bilayer and the complete absence of lead (Pb) penetration into the steel substrate.

The elemental maps of the substrate constituents (Ni, Fe, and Mn) reveal a diffuse signal extending into both the chromium layer and the adjacent solidified lead matrix. This corroborates the hypothesis formulated during the planar analysis regarding the outward diffusion of these alloying elements. Remarkably, despite this outward mass transport, no severe depletion zones are visible within the sub-surface region of the Ni map. Most importantly, no accumulation or penetration of lead is detected within the steel substrate. These two observations clearly distinguish the behavior of Coating-Chromia-10 from that of Coating-Chromia-5.

Figure 9.13 presents the EDXS elemental linescan acquired from the region where the coating successfully maintained its adherence to the substrate. The simultaneous accumulation of chromium and oxygen signals, highlighted within the red box, confirms the presence of chromium oxide scale. However, the concurrent detection of a Pb signal suggests that heavy liquid metal may have been incorporated into the outermost portion of this oxide layer. It must be specified that these data should be considered primarily qualitative, as the nominal spatial resolution of the utilized EDXS spectrometer is $1\text{ }\mu\text{m}$, which approaches the physical thickness of the layers being analyzed.

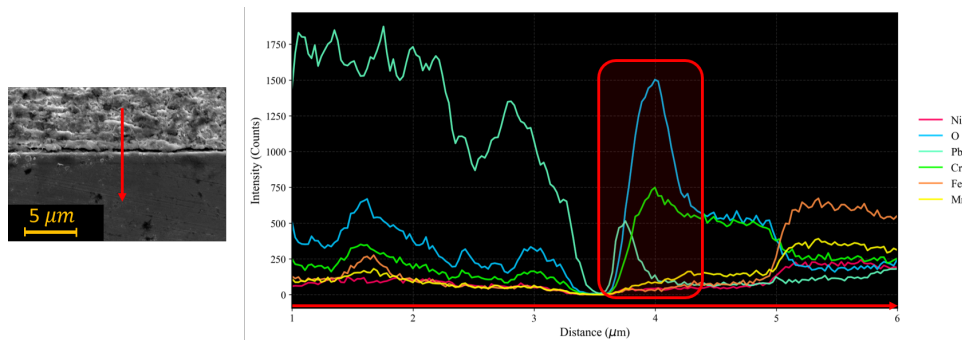


Figure 9.13: Cross-sectional EDXS elemental linescan of the unwashed Coating-Chromia-10 sample in a region where the coating maintained its adherence to the substrate. The red box highlights the interfacial region where the simultaneous accumulation of Pb, Cr, and O suggests the presence of mixed oxides or localized lead incorporation.

9.5. Comparative Evaluation and Physical Interpretation

9.5.1. Corrosion Behavior of the Uncoated Reference Sample

Figure 9.14 presents the cross-sectional SEM micrograph and the corresponding EDXS elemental maps of the uncoated rear surface of the unwashed Coating-Chromia-10 sample.

The SEM micrograph reveals a surface severely altered by corrosion phenomena. The original topography is completely compromised, exhibiting deep, localized pits and craters penetrating up to 10 μm into the substrate.

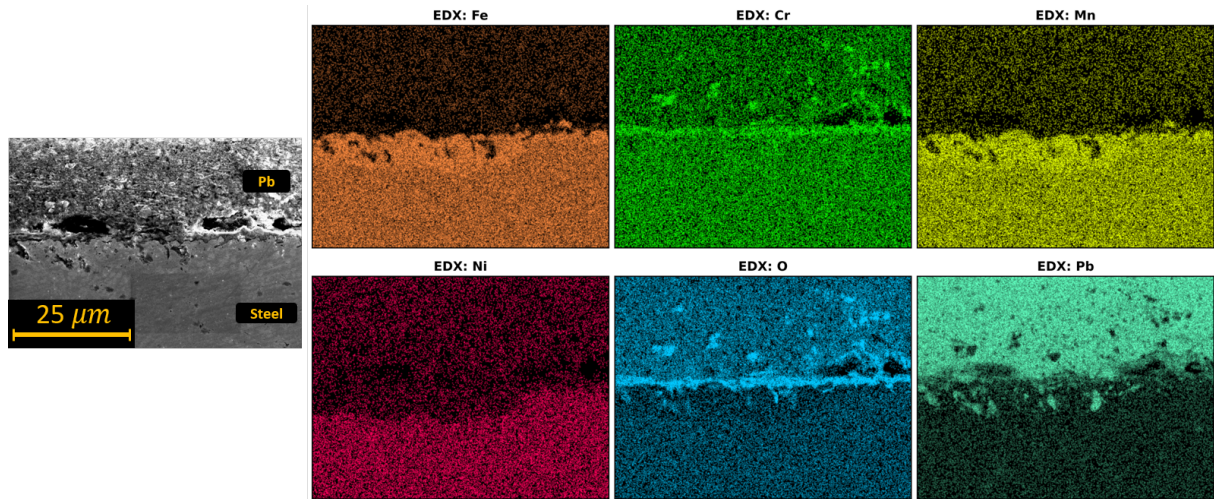


Figure 9.14: Cross-sectional SEM micrograph and corresponding EDXS elemental mapping of the uncoated rear surface (AISI 316L substrate) after 1000 h of exposure to stagnant liquid lead at 600 °C. The elemental distribution highlights the severe degradation of the bare steel.

The EDXS elemental maps clearly illustrate the massive elemental redistribution induced by exposure to the highly corrosive environment. Above the original surface line, a continuous accumulation of Cr and O is detected, indicating the presence of a chromium oxide scale that likely grew during the high-temperature annealing procedure. However, this native scale was entirely insufficient in preventing corrosion. The Fe and Mn maps show an accumulation of signal in the upper 10 μm of the substrate, while a region of similar depth is characterized by severe Ni depletion.

Finally, the Pb map provides unambiguous evidence of liquid metal penetration through localized pits and channels, reaching depths of approximately 10 μm . Interestingly, the areas of maximum Pb infiltration perfectly coincide with the zones of severe Ni depletion. This is highly consistent with the physical mechanisms of liquid metal corrosion, as the penetration of the heavy liquid metal directly drives the preferential dissolution of highly soluble alloying elements, most notably nickel.

It must be noted that this microstructural evolution is not strictly representative of pristine AISI 316L austenitic stainless steel, as the substrate underwent a 10 h thermal treatment at 600 °C in an air muffle furnace, promoting the pre-exposure growth of the aforementioned native oxide scale. Nevertheless, the severe degradation of this surface serves

as a baseline reference to evaluate the enhanced corrosion resistance provided by the engineered bilayer coatings developed in this work.

9.5.2. Comparison and Final Remarks

Now that the experimental framework has been established and all gathered data have been presented, a comparative evaluation can be performed. Two bilayer chromium-based coatings were synthesized and exposed to a stagnant liquid lead pool at the ENEA Brasimone research facility.

Coating-Chromia-5 demonstrated the poorest performance of the two configurations. The thermally grown chromia scale, produced via air annealing at 600 °C for 5 h, completely failed to protect the substrate, as severe Ni dissolution and inward Pb penetration were detected (as shown in the EDXS maps reported in Figure 9.6). The structural morphology of the coating was drastically altered by the action of the high-temperature liquid lead. From the SEM micrographs reported in Figure 9.2E and the planar EDXS maps shown in Figure 9.3, it is evident that the surface of the stainless steel is homogeneously affected by severe pitting corrosion, with craters reaching up to 3 μm in width. Furthermore, the residual, heavily compromised coating was entirely removed during the post-exposure chemical cleaning procedure. Cross-sectional analysis revealed that the average thickness of the residual coating is approximately 1050 nm. This measurement strongly suggests that the outermost oxide scale experienced catastrophic failure under the action of liquid lead (as visible in Figure 9.15b).

Although this configuration offered a slight enhancement in corrosion resistance relative to the bare substrate detailed in Section 9.5.1, the system's overall vulnerability to liquid metal attack remains unacceptably high.

In contrast, Coating-Chromia-10 provided a significant enhancement in the overall corrosion resistance of the system. As shown in the cross-sectional EDXS maps (Figure 9.12), there are no evident signs of lead penetration into the stainless steel substrate and, macroscopically, the bare surface of the substrate shown in figure 9.7b preserved its reflectivity and metallic-behavior. Furthermore, morphological characterization confirms that the coating successfully maintained its bilayer architecture. Figure 9.15a provides a high-magnification cross-sectional view where the red lines delineate the intact intermediate chromium film and the external oxide scale.

From these SEM micrographs, the average thicknesses of the distinct layers were evaluated. The intermediate chromium layer exhibited an average thickness of 945 nm, which, considering measurement uncertainties, remains remarkably consistent with its pristine

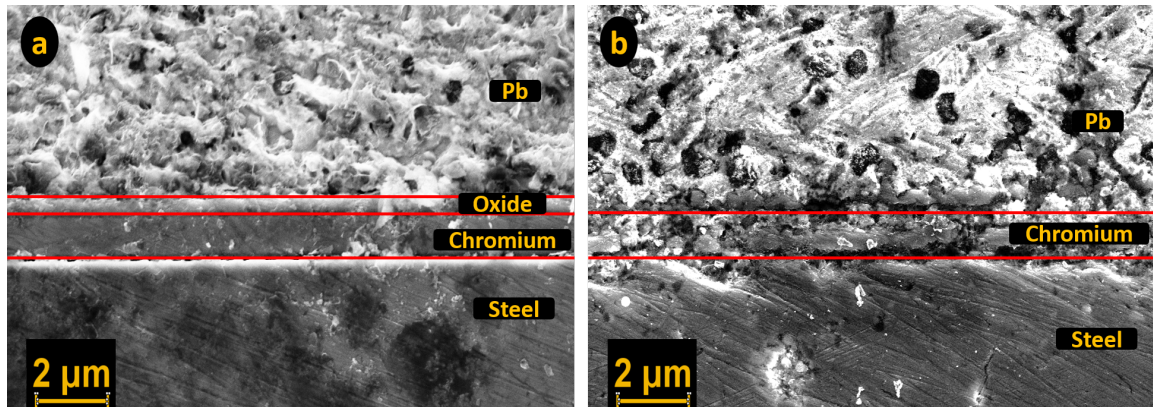


Figure 9.15: (a) Cross-sectional SEM micrograph of the unwashed Coating-Chromia-10 sample in a region where the coating successfully maintained its adherence to the steel substrate. The superimposed red lines delineate the boundaries of the intermediate metallic chromium layer and the outermost thermally grown oxide scale, physically separating the substrate from the adhered solidified lead (Pb). (b) Cross-sectional SEM micrograph of the unwashed Coating-Chromia-5 sample: the structural integrity is severely altered and the oxide scale cannot be identified.

pre-exposure value. Conversely, the external oxide scale measured 516 nm, representing a substantial increase compared to its initial pre-exposure thickness of 125 nm. This growth proves that the coating did not remain inert during the experiments; rather, the oxide scale thickened during exposure due to the outward diffusion of metallic ions from the inner layers of the system. For context, in similar exposure experiments reported by Gong et al. [28], the oxide scales developed on bare structural materials reached tens of micrometers in thickness. This stark contrast further underscores the highly beneficial anticorrosive barrier effect of Coating-Chromia-10.

Despite its successful mitigation of inward lead penetration, the coating did not entirely arrest outward elemental diffusion. As demonstrated by the Raman spectra (Figure 9.9) and EDXS maps (Figures 9.12 and 9.8), substrate alloying elements—namely Fe, Mn, and Ni—diffused through the scale to reach the external surface. Upon contact with the coolant, these elements either formed mixed oxides (such as Fe-Cr spinels) or dissolved directly into the liquid lead. Crucially, the planar morphology of the exposed bare substrate reveals a widespread presence of nano-craters. However, unlike the severe pitting observed in Coating-Chromia-5, the EDXS maps in Figure 9.10 confirm a complete absence of Pb within these nanocavities. Similar nanocavities were also detected on the planar surface of the intermediate chromium layer (Figure 9.7E1). A plausible physical explanation for these pits is the coalescence of vacancies left behind by the outward diffusion of the selec-

tively leached alloying elements. Figure 9.7D1 corroborates this hypothesis, revealing that these nanocavities preferentially nucleate along the substrate's grain boundaries, which inherently act as primary sinks for vacancy agglomeration.

Furthermore, the coating exhibited clear adhesion issues. In the chemically cleaned sample, no traces of the coating were found, whereas in the unwashed sample, the coating easily detached along with the solidified lead upon mechanical removal. Cross-sectional images of the unwashed sample confirm that, in most regions, the coating was still present in the immediate vicinity of the substrate but had completely delaminated. However, even where the coating was detached, the surface of the underlying steel was never found to be directly wetted by the solidified lead. A possible explanation for this phenomenon is that the coating was mechanically pulled away from the substrate by the lead due to severe thermal contraction stresses generated during the cooling and solidification phase. Indeed, this identical behavior was macroscopically observed when the solidified lead flake was manually removed from the unwashed sample. This indicates that a strong interaction occurred between the heavy liquid metal and the protective barrier: the surface of the chromia scale likely exhibited high wettability, possibly allowing the liquid lead to establish a strong bond with the coating that ultimately exceeded the intrinsic interfacial adhesion strength at the substrate-chromium interface.

In conclusion, a comparative analysis of Coating-Chromia-5 and Coating-Chromia-10 reveals a stark divergence in their protective performances. While Coating-Chromia-5 failed to provide substantial improvement over the bare substrate, Coating-Chromia-10 demonstrated a more effective barrier behavior. It managed to halt macroscopic liquid lead penetration and preserved its bilayer architecture, even though it did not completely arrest the outward diffusion of alloying elements during the 1000 h exposure. Unfortunately, both configurations suffered from critical adhesion failures at the chromium-steel interface, ultimately resulting in the complete delamination of the protective barrier.

Given that both coatings possessed comparable thicknesses (100 nm versus 125 nm) and average grain sizes (84 nm versus 95 nm), their drastically different performance cannot be attributed to morphological disparities.

The markedly different corrosion performances cannot be readily explained by differences in oxide thickness or grain size alone, as both parameters remain relatively similar between the two coatings. This suggests that additional microstructural factors, potentially related to defect distribution and oxide quality, may play an important role. The hypothesis is that the root cause lies in their fundamental defect chemistry, as characterized in Chapter 8. The most critical differences between the two systems are the intense photo-

luminescence (PL) signal detected in Coating-Chromia-5 and the formation of interfacial nanovoids in Coating-Chromia-10.

As discussed in Section 8.3, the high PL intensity in the 5 h sample suggests a high density of dispersed crystalline point defects. In the harsh liquid lead environment, these unhealed bulk defects may have acted as fast-diffusion pathways, facilitating the rapid penetration of the heavy liquid metal and the subsequent dissolution of the underlying steel, consistent with what reported by Gong et al. [28]. Conversely, the extended 10 h annealing treatment provided sufficient thermal energy and prolonged exposure to a highly oxidizing atmosphere to drive the system toward a more microstructurally stable state. This extended high-temperature exposure is consistent with a reduction of defect-related features, leading to the formation of interfacial nanovoids. Crucially, these nanovoids did not compromise the internal stability of the coating as the external oxide scale remained firmly adhered to the chromium sublayer. Furthermore, it is reasonable to hypothesize that the oxygen-rich environment promoted the continuous inward diffusion and incorporation of oxygen atoms into the lattice. Such a chemical healing mechanism could effectively balance the stoichiometry of the Cr_2O_3 scale, reducing the defect concentration to a level closer to thermodynamic equilibrium.

Finally, a methodological consideration regarding the chemical cleaning procedure is necessary. The comparison between the washed and unwashed specimens clearly reveals that the utilized cleaning solution drastically altered the post-exposure state of the samples, entirely washing away the protective coatings that had already delaminated due to thermal stresses. Consequently, the preservation and analysis of the unwashed samples proved fundamental for successfully reconstructing the true degradation mechanisms and avoiding severe misinterpretations of the coatings' performance.

Part IV

Conclusions

10 | Conclusions and Future Developments

The main technological barrier to the commercial deployment of Lead-Cooled Fast Reactors (LFRs) is the severe material degradation induced by the heavy liquid metal coolant. To address this, protective thin films have emerged as the most viable near-term mitigation strategy. This project, conducted within the NanoLab research group at Politecnico di Milano, explores the application of chromium-based coatings to fill the existing literature gap regarding their behavior under LFR-relevant conditions. Building on previous group findings, pure metallic chromium deposited via High-Power Impulse Magnetron Sputtering (HiPIMS) was selected as the baseline material. The anticorrosive capability of chromium stems from its ability to develop a robust Cr_2O_3 scale in oxygen-containing environments. Consequently, this experimental work was structured to evaluate the high-temperature oxidation kinetics of HiPIMS-deposited chromium, establish whether thermal annealing is an effective manufacturing strategy for growing high-quality oxide barriers, and subsequently test an engineered bilayer architecture in a stagnant liquid lead pool.

To fulfill the initial objectives of investigating and quantifying the oxidation behavior of HiPIMS-deposited chromium films, an annealing campaign was set up. Three temperature conditions were analyzed (500 °C, 550 °C, and 600 °C) for annealing times of 1 h, 3 h, 5 h and 10 h. The thermally grown oxide scales were analyzed through Scanning Electron Microscopy, Energy Dispersive X-Ray Spectroscopy, Raman spectroscopy, and Photoluminescence (PL) spectroscopy. Continuous, dense chromia scales with nanometric grain sizes were successfully characterized. The grown chromia maintained excellent adhesion to the underlying chromium layer across all conditions, as did the metallic film to the silicon substrates. Multi-wavelength Raman spectroscopy confirmed the high crystallinity and phase purity of the scales, which exhibited compressive stress state. Finally, PL spectra exhibited intense intra-band emissions, which are hypothesized to originate from a high initial density of non-equilibrium point defects; notably, the intensity of these emissions showed a relative reduction for the harshest annealing treatment. By successfully quantifying these properties, the necessary foundation was laid for the subsequent design

phase.

Exploiting this fundamental characterization, the thermal treatments at 600 °C for 5 h (designated as "Coating-Chromia-5") and 10 h (named "Coating-Chromia-10") were selected for testing. These provided the optimal balance of scale thickness and microstructural quality. These optimized bilayer architectures were synthesized on AISI 316L austenitic stainless steel substrates, which serve as standard reference material for LFR core components. Both configurations were subsequently exposed to a stagnant liquid lead pool for 1000 h at an operating temperature of 600 °C, with a dissolved oxygen concentration of 10^{-7} wt%.

By evaluating the coating performance and providing experimental insights into the underlying degradation mechanisms, the post-exposure characterization successfully addressed the initial research questions, revealing a stark divergence in the protective capabilities of the two configurations:

- **Coating-Chromia-5:** This configuration experienced catastrophic failure and demonstrated the poorest performance. The high density of unhealed crystalline point defects, previously suggested by photoluminescence analysis, likely facilitated the diffusion of ions through the scale. It is hypothesized that this structural vulnerability allowed severe inward penetration of liquid lead and dissolution of substrate elements, resulting in deep localized pitting of the substrate and the complete degradation of the protective scale.
- **Coating-Chromia-10:** Conversely, this configuration provided a significant enhancement in overall the corrosion resistance of the system. The extended 10 h annealing treatment improved the crystalline quality, acting to mitigate the fast-diffusion pathways. Consequently, the mature Cr_2O_3 scale appeared effective in halting the macroscopic penetration of liquid lead into the underlying steel and preserved its bilayer architecture. However, the barrier did not completely arrest the outward diffusion of substrate alloying elements (Fe, Ni, and Mn), which migrated through the scale and interacted with the coolant.
- **Interfacial Adhesion Challenges:** Despite the superior microstructural stability of the 10 h configuration, both coatings ultimately suffered from critical interfacial adhesion failures. The highly wettable chromia surface likely established a strong bond with the liquid lead, leading to complete delamination at the chromium-steel interface, which probably occurred during the solidification at the end of the experiment.

In conclusion, the research objectives outlined for this study were successfully accomplished. The experimental campaign comprehensively characterized the microstructural properties of thermally grown chromia scales. The results confirmed that the thermal annealing of HiPIMS-deposited chromium is an effective strategy to grow dense and homogeneous Cr_2O_3 scales. However, the choice of annealing parameters proved to be critical for the final quality of the grown layers. In general, among the tested conditions, longer annealing times at higher temperatures demonstrated the capability to produce scales with the highest crystalline quality.

Furthermore, the liquid lead exposure tests yielded fundamental insights into the underlying degradation phenomena. While the results suggested that a mature, thermally grown Cr_2O_3 scale possesses the potential to act as an effective barrier, they also exposed a stark divergence in performance dictated by the specific annealing conditions. A central insight of this thesis is the strong apparent correlation between the pre-exposure defectivity of the oxide and its subsequent protective efficacy. Specifically, the findings suggest that the initial microstructural maturity of the Cr_2O_3 layer strongly influences the barrier's vulnerability to both inward liquid lead penetration and outward elemental diffusion. Although optimizing the thermal treatment can mitigate these fast-diffusion pathways, persistent outward migration and severe interfacial adhesion failures remain critical hurdles for future development. Finally, from a methodological standpoint, this work highlights that post-exposure chemical cleaning procedures must be carefully calibrated, as aggressive washing can severely compromise data interpretation.

Given these findings and limitations, several potential pathways for future research emerge, aiming to further characterize the studied system and enhance the performance of chromium-based coatings for LFR applications. To advance the technological readiness of chromium-based barriers, future research must focus on:

- **Optimization of Annealing Parameters:** The thermal treatment protocol requires systematic refinement to identify the ideal balance between oxide maturity and thermomechanical stability. Future campaigns should explore a broader parameter space—including varied oxygen partial pressures, intermediate temperatures, and extended durations.
- **Advanced Characterization of Thermally Grown Chromia Scales:** Employ X-Ray Diffraction (XRD) for precise phase profiling alongside defect-sensitive techniques, such as Positron Annihilation Spectroscopy (PAS), to quantitatively map vacancy densities. The electronic properties should be further investigated via UV-Vis spectroscopy, while advanced microstructural topography and cross-sectional analy-

ses require Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM). Concurrently, annealing parameters (e.g., extended annealing times) must be optimized to maximize oxide quality.

- **Quantitative Adhesion Testing:** To address the critical delamination issues, the initial interfacial adhesion strength between the chromium film and the steel substrate must be quantitatively evaluated prior to liquid lead exposure using standardized scratch testing.
- **Advanced Analysis of Corrosion Phenomena:** The baseline corrosion resistance of the coatings should be assessed a priori utilizing experimental techniques such as Electrochemical Impedance Spectroscopy (EIS). Additionally, post-exposure corrosion mechanisms should be corroborated through TEM analysis and XRD measurements.
- **Architectural Upgrades:** Finally, the coating design must be optimized to resolve the critical adhesion failures observed. The introduction of interlayers to enhance chemical bonding and the mechanical compatibility between the chromium layer and the underlying substrate represents a highly promising prospect.

Bibliography

- [1] James J. Duderstadt and Louis J. Hamilton. *Nuclear Reactor Analysis*. John Wiley & Sons, New York. ISBN 978-0-471-22363-4.
- [2] Richard Rhodes. *The Making of the Atomic Bomb*. Simon and Schuster, New York. ISBN 978-1-4516-7761-4.
- [3] International Energy Agency. World Energy Outlook 2025. URL <https://www.iea.org/reports/world-energy-outlook-2025>.
- [4] United Nations Economic Commission for Europe. Life Cycle Assessment of Electricity Generation Options. Carbon Neutrality in the UNECE Region.
- [5] OECD Nuclear Energy Agency and International Atomic Energy Agency. Uranium 2024: Resources, Production and Demand. The Red Book.
- [6] Generation IV International Forum. Gen IV International Forum 2024 Annual Report. URL <https://www.gen-4.org>. Technical Secretariat: OECD/NEA.
- [7] International Atomic Energy Agency. Power Reactor Information System (PRIS), 2026. URL <https://pris.iaea.org/pris/>. World Nuclear Power Status and Statistics.
- [8] Ministero dell'Ambiente e della Sicurezza Energetica. Nucleare sostenibile, Pichetto alla riunione dell'Alleanza: "ruolo strutturale per sicurezza e decarbonizzazione", 2024.
- [9] U.S. Department of Energy. At COP28, Countries Launch Declaration to Triple Nuclear Energy Capacity by 2050, Recognizing the Key Role of Nuclear Energy in Reaching Net Zero, 2023.
- [10] International Atomic Energy Agency. Energy, Electricity and Nuclear Power Estimates for the Period up to 2050. 64th Edition.
- [11] Stephen M Goldberg and Robert Rosner. Nuclear reactors: Generation to generation.

- [12] Ali Ayoub, Haruko M. Wainwright, Giovanni Sansavini, Randall Gauntt, and Kimiaki Saito. Resilient design in nuclear energy: Critical lessons from a cross-disciplinary analysis of the Fukushima Dai-ichi nuclear accident. 27(4):109485. ISSN 25890042. doi: 10.1016/j.isci.2024.109485.
- [13] Hailing Song, Zhen Ma, Peng Song, and Qing Li. Chromium-based coatings and diffusion barriers for accident-tolerant fuel applications. 61(8):5032–5066. ISSN 0022-2461, 1573-4803. doi: 10.1007/s10853-026-12163-7.
- [14] Giorgio Locatelli, Mauro Mancini, and Nicola Todeschini. Generation IV nuclear reactors: Current status and future prospects. 61:1503–1520. ISSN 03014215. doi: 10.1016/j.enpol.2013.06.101.
- [15] Cong Zhang, Ling Chen, Yongfa Zhang, and Song Li. Advancements and development trends in Lead-Cooled Fast Reactor core design. 13(6):1773. ISSN 2227-9717. doi: 10.3390/pr13061773.
- [16] Alexander I. Orlov and Boris A. Gabaraev. Heavy liquid metal cooled fast reactors: peculiarities and development status of the major projects. 9(1):1–18. ISSN 2452-3038. doi: 10.3897/nucet.9.90993.
- [17] Daniele Martelli, Alessandro Del Nevo, Massimo Angiolini, Pietro Agostini, Mariano Tarantino, Giacomo Grasso, Francesco Lodi, Ranieri Marinari, Marco Utili, Camillo Sartorio, Ivan Di Piazza, Dario Diamanti, Serena. Bassini, Sebastiano Cataldo, Pierdomenico Lorusso, Chiara Ciantelli, and Carlo Cristalli. Development of Lead-Cooled Fast Reactor technologies at ENEA Brasimone research center. 50(5):3293–3301. ISSN 2193-567X, 2191-4281. doi: 10.1007/s13369-024-09299-6.
- [18] Vladimir M. Troyanov, Georgy I. Toshinsky, Vladimir S. Stepanov, and Vladimir V. Petrochenko. Lead-bismuth cooled reactors: history and the potential of development. part 1. history of development. 8(3):187–195, . ISSN 2452-3038. doi: 10.3897/nucet.8.93908.
- [19] International Atomic Energy Agency. Challenges for Coolants in Fast Neutron Spectrum Systems, 2020. ISSN 1011-4289. Results of a coordinated research project.
- [20] Steven J. Zinkle and Jeremy T. Busby. Structural materials for fission & fusion energy. 12(11):12–19. ISSN 13697021. doi: 10.1016/S1369-7021(09)70294-9.
- [21] Vladimir M. Troyanov, Georgy I. Toshinsky, Vladimir S. Stepanov, and Vladimir V. Petrochenko. Lead-bismuth cooled reactors: history and the potential of develop-

- ment. part 2. prospects for development. 8(4):237–246, . ISSN 2452-3038. doi: 10.3897/nucet.8.96562.
- [22] Jeong Ik Lee. Review of Small Modular Reactors: Challenges in safety and economy to success. 41(10):2761–2780. ISSN 0256-1115, 1975-7220. doi: 10.1007/s11814-024-00207-0.
- [23] Evgeniy Adamov, Sergey Aleksandrov, Oleg Arkhipov, Dmitriy Afremov, Dmitriy Bakulin, Yuriy Cherepnin, Boris Gabaraev, Igor Danilov, Alexander Dzhalavyan, Sergey Evropin, Andrey Kapliencko, Elena Karandina, Alexey Korostelev, Denis Kulikov, Vadim Lemekhov, Alexander Lopatkin, Alexey Slobodchikov, Yuriy Strebkov, Alexey Umanskiy, and Albert Vasiliev. Innovative projects and technologies of nuclear power engineering. review of proceedings of the VI international scientific and technical conference (ISTC NIKIET-2023) (14–17 november 2023, JSC «NIKIET», Moscow, Russia). 446:114509. ISSN 00295493. doi: 10.1016/j.nucengdes.2025.114509.
- [24] Rosatom Newsletter. Lead-cooled reactor made tangible. URL <https://rosatomnewsletter.com/2023/05/29/lead-cooled-reactor-made-tangible/>. Official publication of the State Atomic Energy Corporation Rosatom.
- [25] T. R. Allen and D. C. Crawford. Lead-cooled fast reactor systems and the fuels and materials challenges. 2007:1–11. ISSN 1687-6075, 1687-6083. doi: 10.1155/2007/97486. URL <http://www.hindawi.com/journals/stni/2007/097486/abs/>.
- [26] newcleo. newcleo: Clean and Safe Nuclear Energy, 2024. URL <https://www.newcleo.com/>. Technical specifications for LFR-AS-30 and LFR-AS-200 systems.
- [27] C. F. Smith, W. G. Halsey, N. W. Brown, J. J. Sienicki, A. Moisseytsev, and D. C. Wade. SSTAR: The US lead-cooled fast reactor (LFR). *Journal of Nuclear Materials*, 376(3):255–259, 2008. doi: 10.1016/j.jnucmat.2008.02.049.
- [28] Xing Gong, Michael P. Short, Thierry Auger, Evangelia Charalampopoulou, and Konstantina Lambrinou. Environmental degradation of structural materials in liquid lead- and lead-bismuth eutectic-cooled reactors. 126:100920. ISSN 00796425. doi: 10.1016/j.pmatsci.2022.100920. URL <https://linkinghub.elsevier.com/retrieve/pii/S0079642522000019>.
- [29] K. Lambrinou, E. Charalampopoulou, T. Van der Donck, R. Delville, and D. Schryvers. Dissolution corrosion of 316L austenitic stainless steels in contact with static liquid lead-bismuth eutectic (LBE) at 500°C. *Journal of Nuclear Materials*, 490:9–27, 2017. doi: 10.1016/j.jnucmat.2017.04.011.

- [30] C. Schroer and J. Konys. Physical chemistry of corrosion and oxygen control in liquid lead and lead-bismuth eutectic. Technical Report FZKA 7364, Forschungszentrum Karlsruhe (FZKA), Karlsruhe, Germany, 2007.
- [31] I. V. Gorynin, G. P. Karzov, V. G. Markov, V. S. Lavrukhin, and V. A. Yakovlev. Structural materials for power plants with heavy liquid metals as coolants. In *Proceedings of the International Conference on Heavy Liquid Metal Coolants in Nuclear Technology (HLMC-98)*, Obninsk, Russian Federation, 1999.
- [32] I. V. Gorynin, G. P. Karzov, V. G. Markov, and V. A. Yakovlev. Structural materials for atomic reactors with liquid metal heat-transfer agents in the form of lead or lead-Bismuth alloy. *Metal Science and Heat Treatment*, 41(9):384–388, 1999. doi: 10.1007/BF02465369.
- [33] K. Lambrinou, V. Koch, G. Coen, J. Van den Bosch, and C. Schroer. Corrosion scales on various steels after exposure to liquid lead-bismuth eutectic. 450(1-3): 244–255. ISSN 0022-3115. doi: 10.1016/j.jnucmat.2013.09.034.
- [34] L. Martinelli, F. Balbaud-Célérier, A. Terlain, S. Delpech, G. Santarini, J. Favergeon, G. Moulin, M. Tabarant, and G. Picard. Oxidation mechanism of a Fe-9Cr-1Mo steel by liquid Pb-Bi eutectic alloy (Part I). 50(9):2523–2536. ISSN 0010-938X. doi: 10.1016/j.corsci.2008.06.019.
- [35] Ronald G. Ballinger and Jeongyoun Lim. An overview of corrosion issues for the design and operation of high-temperature lead- and lead-bismuth - cooled reactor systems. *Nuclear Technology*, 147(3):418 – 435, 2004. doi: 10.13182/NT04-A3540. URL <https://www.scopus.com/inward/record.uri?eid=2-s2.0-5644232381&doi=10.13182%2fNT04-A3540&partnerID=40&md5=c95bd1295d622aad93e4f4bd72118893>. Cited by: 136.
- [36] Valentyn Tsisar, Carsten Schroer, Olaf Wedemeyer, Aleksandr Skrypnik, and Jürgen Konys. Corrosion behavior of austenitic steels 1.4970, 316l and 1.4571 in flowing lbe at 450 and 550°C with 107mass *Journal of Nuclear Materials*, 454(1):332–342, 2014. ISSN 0022-3115. doi: <https://doi.org/10.1016/j.jnucmat.2014.08.024>. URL <https://www.sciencedirect.com/science/article/pii/S0022311514005522>.
- [37] Masatoshi Kondo, Minoru Takahashi, Tadashi Suzuki, Kotaro Ishikawa, Koji Hata, Suizheng Qiu, and Hiroshi Sekimoto. Metallurgical study on erosion and corrosion behaviors of steels exposed to liquid lead–bismuth flow. *Journal of Nuclear Materials*, 343(1):349–359, 2005. ISSN 0022-3115. doi: <https://doi.org/10.1016/j.jnucmat.2004.08.037>. URL <https://www.sciencedirect.com/science/article/>

- pii/S0022311505001480. Proceedings of the 6th International Workshop on Spallation Materials Technology.
- [38] S. P. Lynch. Mechanisms and Kinetics of Environmentally Assisted Cracking: Current Status, Issues, and Suggestions for Further Work. *Metallurgical and Materials Transactions A*, 44(3):1209–1229, 2013. doi: 10.1007/s11661-012-1359-2. URL <https://doi.org/10.1007/s11661-012-1359-2>.
- [39] D. Gorse, T. Auger, J.-B. Vogt, I. Serre, A. Weisenburger, A. Gessi, P. Agostini, C. Fazio, A. Hojna, F. Di Gabriele, J. Van Den Bosch, G. Coen, A. Almazouzi, and M. Serrano. Influence of liquid lead and lead–bismuth eutectic on tensile, fatigue and creep properties of ferritic/martensitic and austenitic steels for transmutation systems. *Journal of Nuclear Materials*, 415(3):284–292, 2011. ISSN 0022-3115. doi: <https://doi.org/10.1016/j.jnucmat.2011.04.047>. URL <https://www.sciencedirect.com/science/article/pii/S0022311511004065>. Proceedings of the International DEMETRA Workshop on Development and Assessment of Structural Materials and Heavy Liquid Metal Technologies for Transmutation Systems.
- [40] A.Yu. Legkikh, R.Sh. Askhadullin, and R.P. Sadovnichiy. Ensuring the corrosion resistance of steels in heavy liquid metal coolants. *Nuclear Energy and Technology*, 2(2):136–141, 2016. ISSN 2452-3038. doi: <https://doi.org/10.1016/j.nucet.2016.05.012>. URL <https://www.sciencedirect.com/science/article/pii/S2452303816300486>.
- [41] Jian Wang, Shanping Lu, Lijian Rong, and Dianzhong Li. Effect of silicon contents on the microstructures and mechanical properties of heat affected zones for 9cr2wvta steels. *Journal of Nuclear Materials*, 470:1–12, 2016. ISSN 0022-3115. doi: <https://doi.org/10.1016/j.jnucmat.2015.11.055>. URL <https://www.sciencedirect.com/science/article/pii/S0022311515303627>.
- [42] K.L. Murty and I. Charit. Structural materials for gen-iv nuclear reactors: Challenges and opportunities. *Journal of Nuclear Materials*, 383(1):189–195, 2008. ISSN 0022-3115. doi: <https://doi.org/10.1016/j.jnucmat.2008.08.044>. URL <https://www.sciencedirect.com/science/article/pii/S0022311508004960>. Advances in Nuclear Materials: Processing, Performance and Phenomena.
- [43] F. García Ferré, M. Ormellese, F. Di Fonzo, and M.G. Beghi. Advanced al2o3 coatings for high temperature operation of steels in heavy liquid metals: a preliminary study. *Corrosion Science*, 77:375–378, 2013. ISSN 0010-938X. doi:

- <https://doi.org/10.1016/j.corsci.2013.07.039>. URL <https://www.sciencedirect.com/science/article/pii/S0010938X13003491>.
- [44] F. García Ferré, A. Mairov, D. Iadicicco, M. Vanazzi, S. Bassini, M. Utili, M. Tarantino, M. Bragaglia, F.R. Lamastra, F. Nanni, L. Ceseracciu, Y. Seruys, P. Trocellier, L. Beck, K. Sridharan, M.G. Beghi, and F. Di Fonzo. Corrosion and radiation resistant nanoceramic coatings for lead fast reactors. *Corrosion Science*, 124:80–92, 2017. ISSN 0010-938X. doi: <https://doi.org/10.1016/j.corsci.2017.05.011>. URL <https://www.sciencedirect.com/science/article/pii/S0010938X16313361>.
- [45] Hao Shi, Adrian Jianu, Alfons Weisenburger, Chongchong Tang, Annette Heinzl, Renate Fetzler, Fabian Lang, Robert Stieglitz, and Georg Müller. Corrosion resistance and microstructural stability of austenitic Fe–Cr–Al–Ni model alloys exposed to oxygen-containing molten lead. *Journal of Nuclear Materials*, 524:177–190, 2019. ISSN 0022-3115. doi: <https://doi.org/10.1016/j.jnucmat.2019.06.043>. URL <https://www.sciencedirect.com/science/article/pii/S0022311519301394>.
- [46] A. Weisenburger, A. Heinzl, G. Müller, H. Muscher, and A. Rousanov. T91 cladding tubes with and without modified FeCrAlY coatings exposed in LBE at different flow, stress and temperature conditions. *Journal of Nuclear Materials*, 376:274–281, 2008. ISSN 0022-3115. doi: [10.1016/j.jnucmat.2008.02.026](https://doi.org/10.1016/j.jnucmat.2008.02.026).
- [47] Junkai Liu, Martin Steinbrück, Mirco Große, Ulrike Stegmaier, Chongchong Tang, Di Yun, Yanguang Yang, Jianqiao und Cui, and Hans Jürgen Seifert. Systematic investigations on the coating degradation mechanism during the steam oxidation of Cr-coated Zry-4 at 1200 °C. *Corrosion Science*, 202:110310, 2022. ISSN 0010-938X. doi: [10.1016/j.corsci.2022.110310](https://doi.org/10.1016/j.corsci.2022.110310).
- [48] Shuangqi Guo, Jinsuo Zhang, Hua Wang, and Detao Yang. Effect of vacuum annealing on the microstructure and corrosion resistance of Cr coatings in liquid Pb. *Surface and Coatings Technology*, 492:130985, 2024. ISSN 0257-8972. doi: [10.1016/j.surfcoat.2024.130985](https://doi.org/10.1016/j.surfcoat.2024.130985).
- [49] L. Latu-Romain, Y. Parsa, S. Mathieu, M. Vilasi, and Y. Wouters. Chromia Scale Thermally Grown on Pure Chromium: Characteristics and Methodological Aspects. *Oxidation of Metals*, 87:363–377, 2017. ISSN 0030-770X. doi: [10.1007/s11085-016-9683-1](https://doi.org/10.1007/s11085-016-9683-1).
- [50] Hans-Joachim Lunk. Discovery, properties and applications of chromium and

- its compounds. *ChemTexts*, 1(1):5, 2014. ISSN 2199-3793. doi: 10.1007/s40828-014-0005-z.
- [51] Nanotrùn. Chromium (Cr) Metal and Compounds: Properties, Applications, and Specifications, 2024. URL <https://www.nanotrùn.com/>. Accessed: 2026-04-27.
- [52] K. Khojier, H. Savaloni, and M. S. Dehnavi. Structural, mechanical and tribological properties of annealed chromium oxide thin films. *Applied Surface Science*, 281:304–309, 2013. ISSN 0169-4332. doi: 10.1016/j.apsusc.2013.06.012.
- [53] François Lebreau, Mazharul M. Islam, Boubakar Diawara, and Philippe Marcus. Structural, Magnetic, Electronic, Defect, and Diffusion Properties of Cr₂O₃: A DFT+U Study. *The Journal of Physical Chemistry C*, 118:18133–18145, 2014. ISSN 1932-7447. doi: 10.1021/jp5039943.
- [54] Li Wang, Qing Liao, Jintao Zhang, Sijie Liu, Shuyun Gan, and Wang. Corrosion behavior of Cr coating on ferritic/martensitic steels in liquid lead-bismuth eutectic at 600 °C and 700 °C. *Journal of Materials Research and Technology*, 29:3958–3966, 2024. ISSN 2238-7854. doi: 10.1016/j.jmrt.2024.02.146.
- [55] Shuwei Guo, Lintao Liu, Fei He, and Shaopeng Wang. Preparation of Cr-N coatings on 316H stainless steel via pack chromizing and gas nitriding, and their resistance to liquid metal corrosion in early stages. *Surface and Coatings Technology*, 481:130665, 2024. ISSN 0257-8972. doi: 10.1016/j.surfcoat.2024.130665.
- [56] Nairu He, Li Ji, Xiaohong Liu, Hongxuan Li, Huidi Zhou, and Jianmin Chen. Role of annealing temperatures on the evolution of microstructure and properties of Cr₂O₃ films. *Applied Surface Science*, 357:1472–1480, 2015. ISSN 0169-4332. doi: 10.1016/j.apsusc.2015.10.021.
- [57] Pankaj Bhardwaj, Jarnail Singh, Rajesh Kumar, Dinesh Kumar, Vikram Verma, and Ravi Kumar. Oxygen defects induced tailored optical and magnetic properties of fexcr₂-xo₃ ($0 \leq x \leq 0.1$) nanoparticles. *Applied Physics A*, 128:135, 2022.
- [58] Brian D. Hosterman. *Raman Spectroscopic Study of Solid Solution Spinel Oxides*. PhD thesis, University of Nevada, Las Vegas, 2011. URL <http://dx.doi.org/10.34917/2476131>.
- [59] T. Larbi, B. Ouni, A. Gantassi, K. Doll, M. Amlouk, and T. Manoubi. Structural, optical and vibrational properties of Cr₂O₃ with ferromagnetic and antiferromagnetic order: A combined experimental and density functional theory study. *Journal*

- of Magnetism and Magnetic Materials*, 444:16–22, 2017. ISSN 0304-8853. doi: 10.1016/j.jmmm.2017.07.100.
- [60] J. Mougin, T. Le Bihan, and G. Lucazeau. High-pressure study of Cr_2O_3 obtained by high-temperature oxidation by x-ray diffraction and raman spectroscopy. *Journal of Physics and Chemistry of Solids*, 62:553–563, 2001.
- [61] I. R. Beattie and T. R. Gilson. The single-crystal raman spectra of nearly opaque materials. iron(iii) oxide and chromium(iii) oxide. *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*, pages 980–986, 1970.
- [62] O. Monnereau, L. Tortet, C. E. A. Grigorescu, D. Savastru, C. R. Iordanescu, F. Guinneton, R. Notonier, A. Tonetto, T. Zhang, I. N. Mihailescu, D. Stanoi, and H. J. Trodahl. Chromium oxides mixtures in pld films investigated by raman spectroscopy. *Journal of Optoelectronics and Advanced Materials*, 12(8):1752–1758, 2010.
- [63] Juan Carlos Idrobo and Libor Kovarik. Electron energy-loss spectroscopy and differential phase contrast imaging with active decision in multimodal electron microscopy: Isotopic detection at the atomic scale. Technical Report PNNL-38640, Pacific Northwest National Laboratory (PNNL), 2025.
- [64] M. Kemdehoundja, J. L. Grosseau-Poussard, J. F. Dinhut, and B. Panicaud. Growth stresses in $\alpha\text{-Cr}_2\text{O}_3$ thermal oxide films determined by in situ high temperature raman spectroscopy. *Journal of Applied Physics*, 2007.
- [65] J Birnie, C Craggs, D.J Gardiner, and P.R Graves. Ex situ and in situ determination of stress distributions in chromium oxide films by raman microscopy. *Corrosion Science*, 33(1):1–12, 1992. ISSN 0010-938X. doi: [https://doi.org/10.1016/0010-938X\(92\)90014-T](https://doi.org/10.1016/0010-938X(92)90014-T). URL <https://www.sciencedirect.com/science/article/pii/0010938X9290014T>.
- [66] M. Mohammadtaheri, Y. Li, J. Corona-Gomez, and Q. Yang. An investigation on synthesis and characterization of superhard Cr-Zr-O coatings. *Surface & Coatings Technology*, 375:694–700, 2019. doi: 10.1016/j.surfcoat.2019.06.102.
- [67] T. Larbi, B. Ouni, A. Gantassi, K. Doll, M. Amlouk, and T. Manoubi. Structural, optical and vibrational properties of Cr_2O_3 with ferromagnetic and antiferromagnetic order: A combined experimental and density functional theory study. *Journal of Magnetism and Magnetic Materials*, 444:16–22, 2017.
- [68] Mohammed K. Khalaf, Dawood salman abd al kader, and Jassim Mohammed salh.

- Annealing effect on structural and optical properties of Cr₂O₃ thin films prepared by R.F magnetron sputtering. *IOP Conference Series: Materials Science and Engineering*, 1105:012064, 2021. doi: 10.1088/1757-899X/1105/1/012064.
- [69] Muftah Al-Mahdawi, Tomohiro Nozaki, Mikihiro Oogane, Hiroshi Imamura, Yasuo Ando, and Masashi Sahashi. Quadratic magnetoelectric effect during field cooling in sputter grown cr₂o₃ films. 2021.
- [70] Gary L. Miessler, Paul J. Fischer, and Donald A. Tarr. *Inorganic Chemistry*. Pearson, 5th edition, 2013.
- [71] A. Stierle and H. Zabel. Oxidation induced roughening during Cr₂O₃(0001) growth on Cr(110). *Surface Science*, 385:167–177, 1997. doi: 10.1016/S0039-6028(97)00257-4.
- [72] Peter A. Mouche, Takaaki Koyanagi, Deep Patel, and Yutai Katoh. Adhesion, structure, and mechanical properties of Cr HiPIMS and cathodic arc deposited coatings on SiC. *Surface & Coatings Technology*, 410:126939, 2021. doi: 10.1016/j.surfcoat.2021.126939.
- [73] R. Auguste, H. L. Chan, E. Romanovskaia, J. Qiu, R. Schoell, M. O. Liedke, M. Butterling, E. Hirschmann, A. G. Attallah, A. Wagner, F. A. Selim, D. Kaoumi, B. P. Uberuaga, P. Hosemann, and J. R. Scully. A multimodal approach to revisiting oxidation defects in Cr₂O₃. *npj Materials Degradation*, 6:61, 2022. doi: 10.1038/s41529-022-00269-7.
- [74] Ali S. Dorcheh, Michael Schütze, and Mathias C. Galetz. Factors affecting isothermal oxidation of pure chromium in air. *Corrosion Science*, 130:261–269, 2018.
- [75] Xiaolu Pang, Kewei Gao, Fei Luo, Huisheng Yang, Lijie Qiao, Yanbin Wang, and Alex A. Volinsky. Annealing effects on microstructure and mechanical properties of chromium oxide coatings. *Thin Solid Films*, 516:4685–4689, 2008. doi: 10.1016/j.tsf.2007.08.083.
- [76] Huseyin Ekinici, Mohammad Soltani, Navid M.S. Jahed, Xiaoli Zhu, Bo Cui, and Dmitry Pushin. Effect of annealing on the structural, optical and surface properties of chromium oxide (Cr₂O₃) thin films deposited by e-beam evaporation for plasma etching applications. *Journal of Alloys and Compounds*, 875:160087, 2021. doi: 10.1016/j.jallcom.2021.160087.
- [77] Benjamin Aronson, Patrick Fourspring, Justin Reiss, Brendan Ensor, Jason Clobes, Lucas Erich, Michael Ammendola, Caillin Ryan, Kelsey Jenkins, Elzbieta Sikora,

- and Douglas Wolfe. Accelerated optimization of chromium coating microstructures for nuclear fuel applications through electrochemical corrosion testing. *Journal of Nuclear Materials*, 585:154628, 2023. ISSN 0022-3115. doi: 10.1016/j.jnucmat.2023.154628.
- [78] Jianqiao Yang, Martin Steinbrück, Chongchong Tang, Mirco Große, Junkai Liu, Jinming Zhang, Di Yun, and Shuzhong Wang. Review on chromium coated zirconium alloy accident tolerant fuel cladding. *Journal of Alloys and Compounds*, 895:162450, 2022. ISSN 0925-8388. doi: 10.1016/j.jallcom.2021.162450.
- [79] Namgook Kim, Hong Hyun Son, and Sung Joong Kim. Oxidation effect on pool boiling critical heat flux enhancement of Cr-coated surface for accident-tolerant fuel cladding application. *International Journal of Heat and Mass Transfer*, 144:118655, 2019. ISSN 0017-9310. doi: 10.1016/j.ijheatmasstransfer.2019.118655.
- [80] Yong-jing Wang, Si-gong Li, Zhi-jia Zhang, Qu-ge Wang, Zhong-xiao Song, and Qian-cheng Zhang. Low-cycle fatigue behavior of zirconium fuel cladding with Cr coatings deposited by High-power Impulse Magnetron Sputtering. *Materials Letters*, 353:135269, 2023. ISSN 0167-577X. doi: 10.1016/j.matlet.2023.135269.
- [81] M.S. Galli De Magistris, D. Vavassori, D. Dellasega, V. Russo, M. Salvi, N. Lecis, A. Smith, A. Milston, M. O’Leary, S. de Moraes Shubeita, F. Currell, M. Passoni, and F. García Ferré. Corrosion behaviour in liquid lead of pristine and irradiated FeCrAlNi coatings deposited by HiPIMS. *Materials & Design*, 260:114923, 2025. ISSN 0264-1275. doi: 10.1016/j.matdes.2025.114923.
- [82] Renate Fetzner, Alfons Weisenburger, Adrian Jianu, and Georg Müller. Oxide scale formation of modified FeCrAl coatings exposed to liquid lead. *Corrosion Science*, 55:213–218, 2012. ISSN 0010-938X. doi: 10.1016/j.corsci.2011.10.019.
- [83] A. Weisenburger, C. Schroer, A. Jianu, A. Heinzl, J. Konys, H. Steiner, G. Müller, C. Fazio, A. Gessi, S. Babayan, A. Kobzova, L. Martinelli, K. Ginestar, F. Balbaud-Célerier, F.J. Martín-Muñoz, and L. Soler Crespo. Long term corrosion on T91 and AISI 316L steel in flowing lead alloy and corrosion protection barrier development: Experiments and models. *Journal of Nuclear Materials*, 415:260–269, 2011. ISSN 0022-3115. doi: 10.1016/j.jnucmat.2011.04.028.
- [84] Jianhui Yu, Xianfeng Ma, and Yu Long. Research progress on the compatibility of high-entropy alloys to high temperature lead-bismuth eutectic: a review. *Nuclear Engineering and Design*, 446:114629, 2026. ISSN 0029-5493. doi: 10.1016/j.nucengdes.2025.114629.

- [85] Tao Liu, Wenguan Liu, Chongdou Yang, Penghui Lei, Di Yun, and Jie Qiu. Corrosion resistance of Cr₂O₃, ZrO₂, and Mn₃O₄ oxide films to lead–bismuth eutectic: A comparative study. *Materials*, 17:5694, 2024. doi: 10.3390/ma17235694.
- [86] Marlene Mühlbacher, Nina Schalk, J. Lu, R. Franz, Christian Mitterer, and Lars Hultman. Enhanced Ti_{0.84}Ta_{0.16}N diffusion barriers, grown by a hybrid sputtering technique with no substrate heating, between Si(001) wafers and Cu overlayers. *Scientific Reports*, 8(1):5360, 03 2018. doi: 10.1038/s41598-018-23649-z.
- [87] Ulf Helmersson, Martina Lattemann, Johan Bohlmark, Arutun P. Eghisarian, and Jon Tomas Gudmundsson. Ionized physical vapor deposition (IPVD): A review of technology and applications. *Thin Solid Films*, 513(1–2):1–24, 2006. doi: 10.1016/j.tsf.2006.03.033.
- [88] Rainer Behrisch. *Sputtering by Particle Bombardment I: Physical Sputtering of Single-Element Solids*, volume 47 of *Topics in Applied Physics*. Springer-Verlag, Berlin, Heidelberg, 1982. ISBN 978-3-540-11071-2. doi: 10.1007/3-540-11071-6.
- [89] Paolo Maria Ossi. *Plasmi per superfici*. Polipress, Milano, Italia, 2006. ISBN 978-88-7398-022-3.
- [90] Peter Sigmund. Theory of sputtering. I. Sputtering yield of amorphous and polycrystalline targets. *Physical Review*, 184(2):383–416, 08 1969. doi: 10.1103/PhysRev.184.383.
- [91] Daniel Lundin, Tiberiu Minea, and Jon Tomas Gudmundsson, editors. *High Power Impulse Magnetron Sputtering: Fundamentals, Technologies, Challenges and Applications*. Elsevier, Amsterdam, Netherlands, 2020. ISBN 978-0-12-812454-3. doi: 10.1016/C2016-0-03046-6.
- [92] K. Sarakinos, J. Alami, and S. Konstantinidis. High power pulsed magnetron sputtering: A review on scientific and engineering state of the art. *Surface and Coatings Technology*, 204(11):1661–1684, 2010. doi: 10.1016/j.surfcoat.2009.11.025.
- [93] Vladimir Kouznetsov, Karol Macak, Jochen M. Schneider, Ulf Helmersson, and Ivan Petrov. A novel pulsed magnetron sputter technique utilizing very high target power densities. *Surface and Coatings Technology*, 122(2–3):290–293, 1999. doi: 10.1016/S0257-8972(99)00447-0.
- [94] Letizia Massari. Investigation by Raman spectroscopy of chromium oxide films for corrosion mitigation in nuclear reactors. Master’s thesis, Politecnico di Milano,

- Milan, Italy, 2025. Scuola di Ingegneria Industriale e dell'Informazione, Corso di Laurea Magistrale in Nuclear Engineering.
- [95] Nanoscience Instruments. Scanning Electron Microscopy: Principles, Techniques, and Applications. <https://www.nanoscience.com/techniques/scanning-electron-microscopy/>, 2026. Accessed: 2026-05-29.
 - [96] Sabu Thomas, Raju Thomas, Ajesh K. Zachariah, and Raghvendra Kumar Mishra, editors. *Spectroscopic Methods for Nanomaterials Characterization*. Micro & Nano Technologies Series. Elsevier, Amsterdam, Netherlands, 2017. ISBN 978-0-323-46140-5.
 - [97] Willes H. Weber and Roberto Merlin, editors. *Raman Scattering in Materials Science*, volume 42 of *Springer Series in Materials Science*. Springer-Verlag, Berlin, Heidelberg, 2000. ISBN 978-3-642-08601-4. doi: 10.1007/978-3-662-04221-2.
 - [98] Edinburgh Instruments Ltd. What is Raman Spectroscopy? <https://www.edinst.com/resource/what-is-raman-spectroscopy/>, 07 2021. Published: July 8, 2021; Accessed: 2025-09-15.
 - [99] S. Khamlich, E. Manikandan, B. D. Ngom, J. Sithole, O. Nemraoui, I. Zorkani, R. McCrindle, N. Cingo, and M. Maaza. Synthesis, characterization, and growth mechanism of α -cr₂o₃ monodispersed particles. *Journal of Physics and Chemistry of Solids*, 72:714–718, 2011.
 - [100] S. Koniakhin, Oleg Utesov, and A. Yashenkin. Raman peak shift and broadening in crystalline nanoparticles with lattice impurities. *Diamond and Related Materials*, 146:111182, 05 2024. doi: 10.1016/j.diamond.2024.111182.
 - [101] M. A. Ibrahim and A. A. El-Amin. Photoluminescence: Fundamentals and Applications. In Ibrahim Dincer, editor, *Comprehensive Energy Systems*, volume 5, pages 412–438. Elsevier, Oxford, UK, 2018. doi: 10.1016/B978-0-12-809597-3.00531-4.
 - [102] Guillaume F. Nataf. *New approaches to understand conductive and polar domain walls by Raman spectroscopy and low energy electron microscopy*. PhD dissertation, Université Paris-Saclay and Université du Luxembourg, Paris, France and Luxembourg City, Luxembourg, 2016. HAL Id: tel-01412787, NNT: 2016SACLS436.
 - [103] F. García Ferré, C. Pudoyer, A. Ventrella, E. Virgillito, L. Silvioli, L. Autones, M. Tarantino, A. Barbensi, and L. Cinotti. NEWCLEO's strategy for materials & chemistry: Implementation: team, infrastructure and recent highlights on standard steels, coatings, new materials, chemistry and irradiations. In *Proceedings of the*

- International Conference on Fast Reactors and Related Fuel Cycles (FR26)*, Turin, Italy and Brasimone, Italy, 2026. newcleo s.p.a. and ENEA. Corresponding author: francisco.garcia.ferre@newcleo.com.
- [104] Laura Sanna. Mechanical characterization of chromium thin films for nuclear applications. Master's thesis, Politecnico di Milano, 2024.
- [105] Viola Vaccari. Elastic properties of sub-micrometric chromia coatings for nuclear applications. Master's thesis, Politecnico di Milano, 2025.
- [106] Michael Ammendola, Benjamin Aronson, Patrick Fourspring, Christopher DeSalle, Justin Reiss, Brendan Ensor, Jason Clobes, Kelsey Jenkins, Andrew Payant, Lucas Erich, Ryan Romesberg, Darren Heeman, and Douglas Wolfe. Evaluation of chromium coatings deposited by standard and bipolar high-power impulse magnetron sputtering (hipims & b-hipims) for nuclear power applications. *Surface and Coatings Technology*, 485:130835, 2024. doi: 10.1016/j.surfcoat.2024.130835.
- [107] Neil Birks, Gerald H. Meier, and Frederick S. Pettit. *Introduction to the High Temperature Oxidation of Metals*. Cambridge University Press, 2 edition, 2006. doi: 10.1017/CBO9781139163903.
- [108] Andrea Orlando, Filippo Franceschini, Cristian Muscas, Solomiya Pidkova, Mattia Bartoli, Massimo Rovere, and Alberto Tagliaferro. A comprehensive review on raman spectroscopy applications. *Chemosensors*, 9:262, 2021. doi: 10.3390/chemosensors9090262.
- [109] A. M. Huntz, S. Daghigh, A. Piant, and J. L. Lebrun. Evidence of stress relaxation in thermally grown oxide layers—experiments and modelling. *Materials Science and Engineering: A*, 248:44–55, 1998.
- [110] Amelia Carolina Sparavigna. Raman spectroscopy of the iron oxides in the form of minerals, particles and nanoparticles. *ChemRxiv*, 2023. doi: 10.26434/chemrxiv-2023-22kh4-v2.
- [111] Aleksandra Bendeliani, Felix Kaminsky, Roman Shendrik, and Artem Krivenko. Raman spectroscopic study of inclusions of ferropericlase and other minerals from super-deep diamonds. *Solid Earth Sciences*, 11:100304, 2026. doi: 10.1016/j.sesci.2026.100304.
- [112] Veronica D'Ippolito, Giovanni B. Andreozzi, Danilo Bersani, and Pier Paolo Lottici. Raman fingerprint of chromate, aluminate and ferrite spinels. *Journal of Raman Spectroscopy*, 46(12):1255–1264, 2015. doi: 10.1002/jrs.4764.

- [113] Ilaria Costantini, Pier Paolo Lottici, Kepa Castro, and Juan Manuel Madariaga. Use of temperature controlled stage confocal raman microscopy to study phase transition of lead dioxide (plattnerite). *Minerals*, 10(5):468, 2020. doi: 10.3390/min10050468.

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