



High-temperature lithium transport and phase evolution in amorphous Al_2O_3 exposed to lead–lithium

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ABSTRACT

Ceramic materials exposed to lithium-containing environments are of interest for applications including solid-state electrolytes, electrochemical storage, and fusion reactor systems. In fusion blankets, ceramic coatings deposited on steel substrates must withstand high-temperature operation in contact with lithium-containing coolants while providing chemical stability, electrical insulation, and corrosion protection. This work investigates lithium transport, phase evolution, and chemical stability in ceramic coatings exposed to liquid lead–lithium environments. Amorphous Al_2O_3 coatings deposited by pulsed laser deposition (PLD) on EUROFER97 steel were exposed to static lead–lithium eutectic at 550 °C for up to 7000 h. Coating evolution was investigated by combining X-ray photoelectron spectroscopy (XPS), atom probe tomography (APT), transmission electron microscopy (TEM), and X-ray diffraction analyses with kinetic and thermodynamic modeling. Exposure to lead–lithium induces an amorphous-to-crystalline transition associated with the formation of the lithium-containing ternary phase LiAl_2O_6 . Lithium rapidly diffuses into the alumina coating during early exposure stages, reaching a stable bulk concentration of approximately 3–4 at% after less than 1000 h. A lithium-enriched region develops at the coating–liquid metal interface, while localized lithium accumulation is also observed near the coating–steel interface. Despite lithium incorporation and partial crystallization, no significant lithium penetration into the EUROFER97 substrate is detected. These findings provide new insights into lithium incorporation mechanisms and phase evolution in ceramic coatings exposed to lithium-containing liquid metals, highlighting the importance of advanced characterization techniques for understanding their long-term behavior.

1. Introduction

Ceramics represent a class of materials that has become increasingly relevant for applications involving lithium across several fields of

materials science. By controlling chemical composition and microstructure, lithium-containing ceramics have been extensively investigated as solid-state electrolytes for lithium-ion batteries [1], where the high mobility of the lithium ions can be exploited, as well as for

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electrochemical energy storage applications, in which significant lithium retention can be achieved [2].

Beyond these technologies, other strategic sectors share a strong interest in lithium–ceramic interactions. One prominent example, which is the focus of the present work, is nuclear fusion technology, where lithium plays a significant role due to its nuclear properties when exposed to neutron fluxes.

In fact, when lithium atoms interact with neutrons, tritium (T) can be produced as a nuclear reaction [3]. Tritium is a key component of the deuterium–tritium (D–T) fusion fuel, but its natural availability is intrinsically limited by the instability of its nucleus. To enable the future commercialization of nuclear fusion energy, tritium must therefore be continuously produced. This can be therefore achieved directly within a fusion reactor by exploiting nuclear reactions between DT fusion neutrons and lithium, which is contained in dedicated components known as Breeding Blankets (BB) and located around the vacuum vessel. In this context, lithium can be employed either in the form of solid ceramic breeder pebbles or as a liquid metal, typically a lead–lithium eutectic alloy.

The present work focuses on the latter configuration, specifically within the framework of the Water-Cooled Lead–Lithium (WCLL) Breeding Blanket concept developed by the EUROfusion consortium. While liquid breeder concepts are essential for the development of next-generation fusion reactors such as ITER and DEMO [4–6], they also introduce additional materials engineering challenges.

In the WCLL Breeding Blanket, which is designed to operate at temperatures in the range of 450–550 °C, lithium-containing melts are extremely aggressive towards structural materials. Under the expected operating conditions, the selected Reduced Activation Ferritic–Martensitic (RAFM) steel EUROFER97 has been shown to undergo Heavy Liquid Metal (HLM) corrosion, driven by the solubility of steel alloying elements in lead–lithium, which leads to unacceptably high dissolution rates [7,8].

Moreover, tritium is generated within the flowing liquid metal and transported through the breeding blanket before being extracted in dedicated facilities. At these temperatures, hydrogen isotopes exhibit high mobility and can readily permeate through the RAFM steel microstructure forming the breeding blanket walls. This outward diffusion both reduces the overall efficiency of tritium recovery and extraction [9,10] and increases the safety hazards for the operators [11] and the risk of release in the environment [12].

In addition, at the interface between the flowing liquid metal and the conductive steel walls, magnetohydrodynamic effects induced by the presence of strong magnetic fields can significantly increase flow resistance, resulting in higher pumping power requirements [13,14].

Overall, the application of an anti-corrosion, anti-permeation and electrically-insulating barrier layer on the surface of EUROFER97 has been proposed as an effective strategy to mitigate these issues, while avoiding the need for advanced and costly structural alloys [15,16]. Among the candidate coating materials, alumina (Al_2O_3) has emerged as a particularly promising solution [17].

When deposited by Pulsed Laser Deposition (PLD), Al_2O_3 thin films can be obtained with an amorphous microstructure. This feature has been associated with enhanced ductility and mechanical stability under thermal cycling [18,19], chemical compatibility with heavy liquid metals [20,21], radiation tolerance [20,22–24], low hydrogen isotope permeability [25,26], and high electrical resistivity [27]. The combination of these properties makes amorphous PLD alumina coatings particularly attractive for improving the functional performance and lifetime of steel components operating in liquid metal environments.

Nevertheless, it is known that the exposure of alumina to lead–lithium at high temperature can promote lithium incorporation into the coating and the formation of lithium aluminate phases, such as LiAlO_2 [28–30]. While this interaction does not compromise the corrosion protection of the underlying steel, lithium uptake modifies the coating microstructure and may degrade its anti-permeation

performance. Early works identified the formation of these phases and their stoichiometry, but they did not provide a detailed characterization of the lithium concentration profile within the coating [31]. A recent study has addressed this gap by a multi-technique approach that involved Nuclear Reaction Analysis (NRA), X-ray diffraction (XRD), and Atom Probe Tomography (APT) [32]. Thanks to this strategy, it was possible to quantify, for the first time, the Li content and depth distribution in Al_2O_3 coatings, showing an inhomogeneous profile with higher concentrations at the surface and at the coating/steel interface. X-ray diffraction confirmed the formation of Al–Li mixed oxides, and APT revealed nanoscale Li-rich domains near the interface, highlighting the interface as a previously uncharacterized region of Li accumulation.

This evidence has critical implications under fusion-relevant conditions, as neutronic calculations for DCLL and WCLL breeder blanket concepts showed that Li-rich regions, particularly at the surface and at the coating/steel interface, could act as concentrations of helium generation, potentially affecting coating integrity, adhesion, and long-term performance [33,34].

While these works provided important insights into the composition and distribution of Li, several critical aspects remain unexplored. In particular, the mechanisms driving Li transport, its impact on coating performance, and its interaction under realistic operational conditions are not yet fully understood.

Building on these findings, the present work further investigates Li transport and accumulation at the coating/steel interface, employing advanced characterization to provide a more detailed understanding of the lithiation mechanism. This is essential for designing coatings capable of maintaining performance under the complex conditions of fusion reactors, and for establishing robust protocols for experimental reproducibility.

To reproduce conditions relevant to WCLL Breeding Blanket operation, PLD-coated EUROFER97 samples were exposed to lead–lithium under static corrosion conditions at 550 °C. In the attempt to evaluate the reaction kinetics, the samples were immersed for different periods of time (1000 h, 4000 h, and 7000 h). Post-exposure characterization was performed using energy-dispersive X-ray spectroscopy (EDS) for the detection of heavy elements and lead-based compounds, while transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) were employed to investigate microstructural modifications and crystalline phase formation. For accurate lithium detection, several advanced techniques were evaluated, with X-ray photoelectron spectroscopy (XPS) and APT proving particularly effective. Through optimized sample preparation and measurement strategies, lithium concentration profiles with high spatial resolution across the coating thickness were obtained. Thermodynamic calculations were also conducted to support experimental observations by assessing the stability of alumina and lithium-containing compounds.

Beyond the specific nuclear fusion application, the results of this study contribute to a broader understanding of lithium–ceramic interactions in amorphous oxide systems at elevated temperature, providing insights of general relevance to the materials science community.

2. Experimental

2.1. Preparation of coated specimens

ENEA provided EUROFER97 steel substrates that were machined into plates ($30 \times 10 \times 1 \text{ mm}^3$).

Prior to the application of the coating, the steel plate surfaces were ground with SiC abrasive paper and polished with diamond particle suspensions to achieve an average surface roughness $< 100 \text{ nm}$. The steel samples were ultrasonically cleaned in acetone and isopropanol, rinsed, and dried with pressurized nitrogen before mounting in the vacuum chamber for the deposition of the coating material.

In-situ plasma cleaning with Ar⁺ ions was applied to eliminate

residual contaminations from the organic solvent bath from the surface of the steel.

For the PLD process, a COMPexPRO 205 F KrF laser was used (Coherent GmbH), which produces a laser radiation at 248 nm wavelength at a pulse repetition rate of 50 Hz. The Al_2O_3 coating material was ablated from a polycrystalline alpha- Al_2O_3 target (Testbourne Ltd®, 99.99% purity). The PLD deposition was conducted in a reactive atmosphere with 0.15 Pa of oxygen partial pressure and without an active heating of the substrate material.

2.2. Corrosion tests in liquid lead-lithium

The corrosion tests were conducted in the RACHEL experimental setup present at the ENEA Brasimone Research Centre.

Coated EUROFER97 samples were placed within thermally insulated stainless-steel capsules, with the samples placed inside an alumina crucible. Heating elements were wrapped around the outer surface of the capsules to heat the lead-lithium to the desired temperature. Each sample had a hole at one end to hang from specimen-holder bars using screws, nuts, and washers. These components were made of tungsten (W), selected because this refractory metal is insoluble in molten lead-lithium.

The eutectic alloy was introduced into the crucible in its molten state using a melting tank operating under slight argon overpressure (99.9999% purity).

The samples were initially immersed at approximately 300 °C, and the lead-lithium was then heated to 550 °C at a rate of 1 °C/min.

A slight argon cover gas overpressure was maintained in the capsules to prevent air ingress. This procedure was intended to ensure that the tests were conducted far from the oxygen solubility limit of the melt. However, due to lithium's high tendency to oxidize even with minimal oxygen contamination, complete avoidance of oxygen saturation in practice is challenging.

A more detailed description of the experimental setup used for the static corrosion test is available in previously published works [7].

2.3. Post-exposure characterization methods

For the microstructural analysis, cross-sectional TEM specimens were prepared using the focused ion beam lift-out technique, enabling site-specific extraction of lamellae from the coating before and after exposure [35]. The region of interest was first identified using SEM imaging within the dual-beam system, after which a protective platinum layer was deposited to prevent surface damage during milling. Two trenches were then milled alongside the Pt strip using a high ion current, leaving a thin wall of material that was subsequently thinned to electron transparency. The lamella was kept attached at its upper corners during most of the fabrication to maintain mechanical stability before final lift-out and mounting. Analytical TEM investigations were primarily conducted at the Institute for Applied Materials (IAM), Karlsruhe Institute of Technology (KIT), using a ThermoFisher Talos F200XG2 operated at 200 kV. The instrument is equipped with four windowless SDD detectors (total solid angle ~0.9 sr) for high-throughput STEM/EDX analysis and a Gatan Enfium Dual spectrometer for electron energy-loss spectroscopy (EELS). All lamellae were plasma-cleaned for 10–20 min prior to analysis to reduce hydrocarbon contamination. Additional TEM and SAED analyses were conducted at UKAEA using a JEOL NEOARM microscope operated at 200 kV. This instrument is equipped with a cold-FEG electron source and a standard selected-area diffraction aperture, enabling high-contrast imaging and reliable acquisition of diffraction patterns from localized regions of the coating and the interface. These complementary measurements provided independent confirmation of the structural features observed in the Talos analyses and supported cross-validation of crystallographic and microstructural results.

Selected-Area Electron Diffraction (SAED) patterns were also

acquired to assess the crystallographic structure of the coatings and to identify potential structural changes induced by the elevated temperature corrosion test. SAED analysis was performed both on pristine regions and across interface areas, enabling the differentiation between amorphous and crystalline phases and the detection of any local ordering or phase transformation.

To complement the crystallographic information obtained by SAED, Grazing Incidence X-Ray Diffraction (GI-XRD) measurements were performed in grazing incidence geometry. While SAED provides local diffraction patterns from nanometer-scale regions probed by the electron beam, GI-XRD enables a volumetric assessment of the near-surface crystalline structure using a distinct scattering source. The combination of the two techniques therefore allows cross-validation of the phase composition and the identification of possible structural changes in the upper layers of the coating after interaction with liquid lead-lithium. GI-XRD measurements were conducted using a Bruker D8 Advance diffractometer equipped with a $\text{Cu K}\alpha$ radiation source and keeping a grazing incidence angle of 1° between the source and the sample. This configuration was selected to investigate the phase distribution and microstructure of the coatings before and after Pb–Li exposure, with enhanced surface sensitivity suitable for detecting modifications in the outermost layers. Crystallography Open Database (COD) was consulted for the identification of crystalline phases [36].

Energy-Dispersive X-ray Spectroscopy (EDX), commonly integrated into both SEM and TEM systems, was selected as a quick and efficient technique to discriminate chemical modifications that could have involved elements heavier than lithium. EDX was applied to cross-sectional lamellae, allowing compositional analysis across the coating thickness and interfaces with minimal beam broadening, yielding high-quality lateral and depth-resolved elemental maps. The very low energies of the lithium characteristic X-rays (<100 eV) result however in strong attenuation and place them below the practical detection range of standard detectors. Consequently, lithium quantification required alternative techniques with higher sensitivity to light elements. Despite this limitation, EDX provides complementary information to structural imaging and high-resolution analytical methods, supporting the correlation between microstructural features and local chemical variations. Analytical STEM/EDX measurements were conducted on both pristine and exposed samples at the Institute for Applied Materials (IAM), Karlsruhe Institute of Technology (KIT).

Sputtering-assisted X-ray Photoelectron Spectroscopy (XPS) was employed to obtain lithium concentration profiles across the coating cross section. Spectra were acquired over a 300 $\mu\text{m} \times 700 \mu\text{m}$ analysis area using a pass energy of 40 eV. Chemical composition profiles were obtained by alternating Ar^+ sputtering cycles (4 keV ion energy over a 3 $\times$ 3 mm² area) with XPS acquisition at the centre of the sputtered region. To assess the reliability of this XPS depth profiling technique and to exclude possible instrumental artifacts, a dedicated set of reference samples was prepared and analyzed under the same experimental conditions adopted for the lead-lithium exposed coatings (see [Supplementary Materials](#) for more details on the procedure). The O 1 s, C 1 s, Pb 4 f, Al 2p, Fe 2p, and Li 1 s core levels were monitored throughout the sequence. The sputtering rate was calibrated to convert sputtering time into erosion depth, assuming a linear correlation between time and removed thickness. Depth profiling continued until the appearance of the Fe 2p peak indicated that the Al_2O_3 layer had been fully etched. XPS depth profiling was conducted using a Kratos Axis Ultra^{DLD} spectrometer equipped with a monochromatic Al $\text{K}\alpha$ source (20 mA, 15 kV). Nevertheless, the reliable detection of lithium was limited by the spectral overlap between the Li 1 s and Fe 3p peaks and by the differing relative sensitivity factors of these signals. As a result, Li became increasingly difficult to detect once Fe was exposed during sputtering. For this reason, APT was subsequently used to achieve higher spatial resolution and improved sensitivity in the coating–steel interfacial region. For the APT investigations, three complementary lift-out strategies were adopted to obtain a comprehensive picture of lithium incorporation after the

corrosion test (see [Supplementary Materials](#)). The first specimen (APT Set 1) was extracted from the outer surface of Sample 3–4000. A 100 nm Au layer was sputter-deposited prior to lift-out to serve as a fiducial marker for the external surface [37]. This dataset was designed to probe the Li concentration at the surface and within the first few micrometers of the coating. The second specimen (APT Set 2) was lifted out from a polished cross-section of Sample 3–7000 to capture lithium concentration profiles at different depths and to extend the analysis into the underlying steel substrate. For this lift-out, a Cr capping layer was applied following established procedures widely used in Li-ion battery research, to enhance Li retention and improve mass-spectral quality. The third specimen (APT Set 3) was extracted from a polished cross-section of Sample 3–7000 with the specific objective of resolving the Li distribution in the coating region immediately adjacent to the steel interface. All APT specimens were prepared using standard site-specific lift-out procedures on an FEI Versa 3D FIB/SEM dual-beam workstation. APT Set 1 was analyzed using a CAMECA LEAP 3000X HR at 45 K, with a laser pulse energy of 0.4 nJ, an evaporation rate of 0.15%, and a pulse frequency of 100 kHz. APT Set 2 was analyzed using a CAMECA LEAP 6000 XR at 50 K, with a laser pulse energy of 80–100 pJ, an evaporation rate of 0.3%, and a pulse frequency of 200 kHz. APT Set 3 was analyzed using a CAMECA LEAP 5000 XR, laser energy of 85 pJ, target evaporation rate 0.2%, and pulse frequency of 200 kHz.

Additional compositional analyses were performed using ion beam techniques (ERDA, NRA and RBS) and ToF-SIMS. The corresponding experimental details and results are reported in the [Supplementary Material](#).

3. Results

3.1. As-deposited Al_2O_3 thin films

The as-deposited Al_2O_3 coating exhibits a uniform and compact morphology throughout its thickness. Bright-field (BF) TEM imaging ([Fig. 1](#)) reveals that the microstructure of the film is uniform and

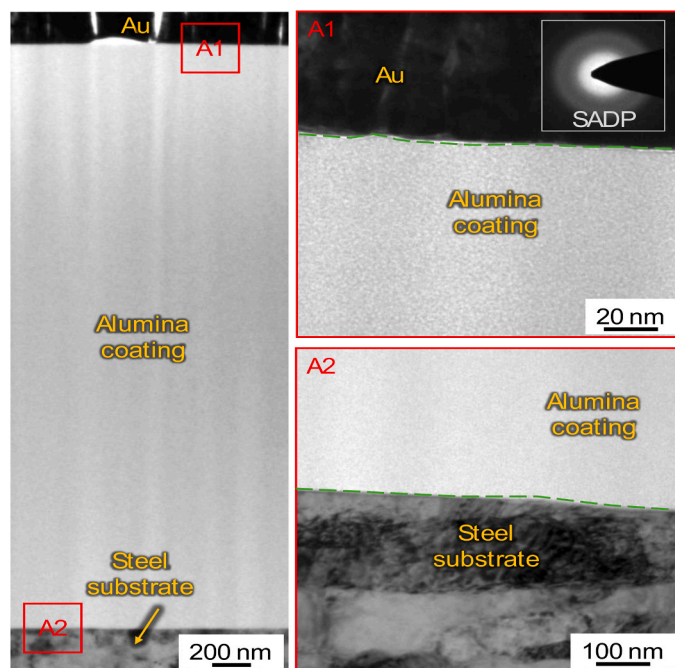


Fig. 1. BF-TEM image of the as-deposited Al_2O_3 sample; close-up view of the coating outer surface covered in a gold protective layer, marked Au (Box A1) and of the coating-steel interface (Box A2). A selected area diffraction pattern collected from the amorphous alumina coating is displayed in the grey SADP Box.

compact, with no evidence of structural inhomogeneities such as crystalline domains or grain boundaries. Vertical streaks in the image are from artefacts from the FIB preparation. This observation is consistent with the SAED pattern obtained from the coating, which shows a diffuse diffraction ring characteristic of a fully amorphous PLD-deposited alumina layer. BF images at higher resolution acquired in the proximity of the outer free surface (Box A1) and at the interface with the EUROFER97 substrate (Box A2), do not show any alteration of the coating microstructure.

The microstructure of the underlying EUROFER97 substrate is still unaltered, displaying the expected martensitic lath structure and the characteristic distribution of M_{23}C_6 , VN, and TaC precipitates. No additional phases or microstructural modifications attributable to the coating process were detected.

The composition of the coating and the EUROFER97 substrate was evaluated through STEM-EDX elemental mapping ([Fig. 2](#)). The PLD-deposited thin film demonstrates to be uniform also in elemental distribution, with EDX signals associated with oxygen ($K_{\alpha,\text{O}} = 0.525$ keV) and aluminum ($K_{\alpha,\text{Al}} = 1.486$ keV) emission lines found to be the only contribution throughout the entire thickness, with no detectable segregation or compositional gradients ([Fig. 2b,c](#)). No other elements were identified within the coating. The EUROFER97 steel substrate shows uniform distribution of the iron peak ($K_{\alpha,\text{Fe}} = 6.398$ keV), chromium ($K_{\alpha,\text{Cr}} = 5.414$ keV), and other main alloying elements at levels consistent with the composition of the RAFM steel. Nevertheless, at the coating-substrate interface, a thin manganese-rich layer approximately 50 nm thick is seen ([Fig. 2e](#)). Moreover, a distribution of small aggregates of vanadium ($K_{\alpha,\text{V}} = 4.949$ keV) is detected, and a thin (5–10 nm) V-enriched layer is present ([Fig. 2g](#)). This could be attributed to the formation of a thin passivation layer formed on the surface prior to deposition. This behavior, typically accompanied by the local enrichment in elements such as Mn, Cr, and V, has been reported to occur in similar steels as a consequence of the polishing procedure and subsequent oxidation [38,39].

XPS depth profiling of a reference alumina coating deposited under the same conditions showed an average composition of approximately 43 at% Al and 57 at% O, corresponding to an O/Al atomic ratio of approximately 1.35, slightly below the stoichiometric value of 1.5 for Al_2O_3 . Further details on the XPS characterization and depth-profile calibration are provided in the [Supplementary Material](#).

3.2. Post-exposure condition

As reference sample to prove the effect of the lead-lithium exposure at 550 °C, the complete analysis set has been carried out on the sample immersed in lead-lithium for 7000 h, the longest exposure time investigated. Bright Field TEM images of the Al_2O_3 coating ([Fig. 3](#)) evidence that the thin film during exposure undergoes a structural modification. The as-deposited amorphous state has been replaced by nanocrystalline domains dispersed throughout the entirety of the coating thickness. Crystalline domains appear with varied contrast because the BF-TEM imaging is also governed by diffraction effects which depend on the crystal-beam orientation and thickness. Long-range atomic order in the crystalline regions gives Bragg diffraction, leading to a variation in the diffracted beams, whereas the amorphous matrix contributes to diffuse scattering with more even contrast. These crystalline grains are heterogeneously distributed and randomly oriented but are consistently present at all depths ([Fig. 3](#)). No systematic measurement of the crystal texture was made. These grains exhibit variable sizes, with coarser crystallites located near the outer surface and increasingly finer grains towards the coating-steel interface.

On the outer surface of the coating, a compact and homogeneous layer approximately 100 nm thick is seen ([Fig. 3, Box B1](#)). This surface layer contains crystals more densely packed than those found deeper in the coating.

Within the first few tens of nanometers in the coating from the

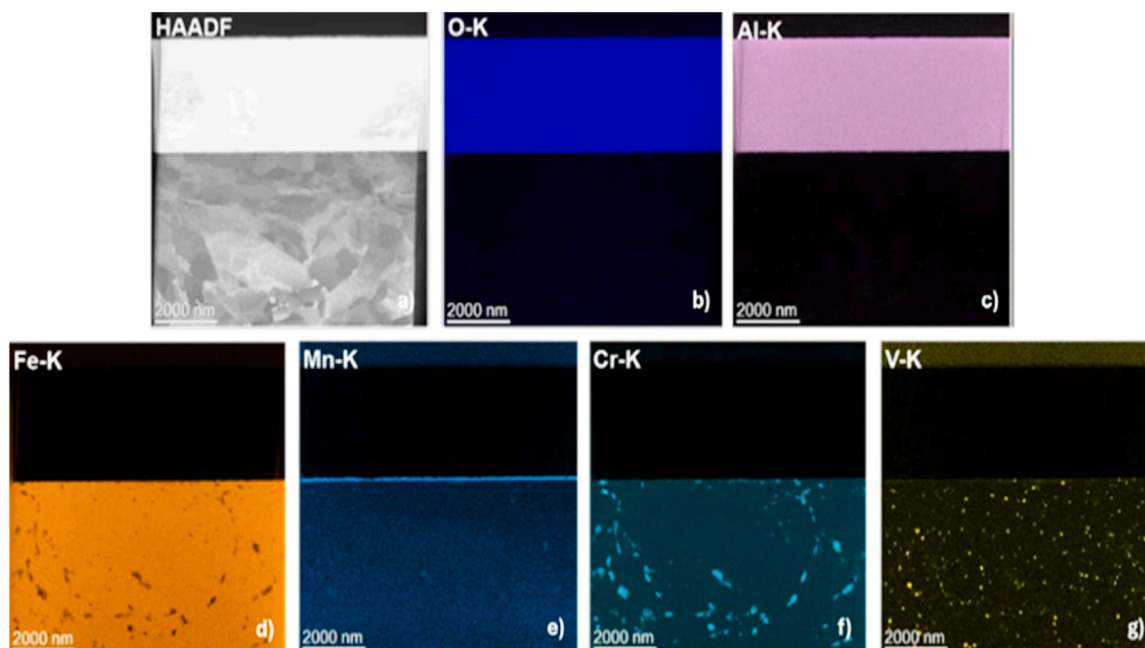


Fig. 2. STEM/EDX elemental maps (O, Al, Fe, Mn, Cr, V) of as deposited 3 μm thick PLD deposited Al_2O_3 coating on EUROFER97.

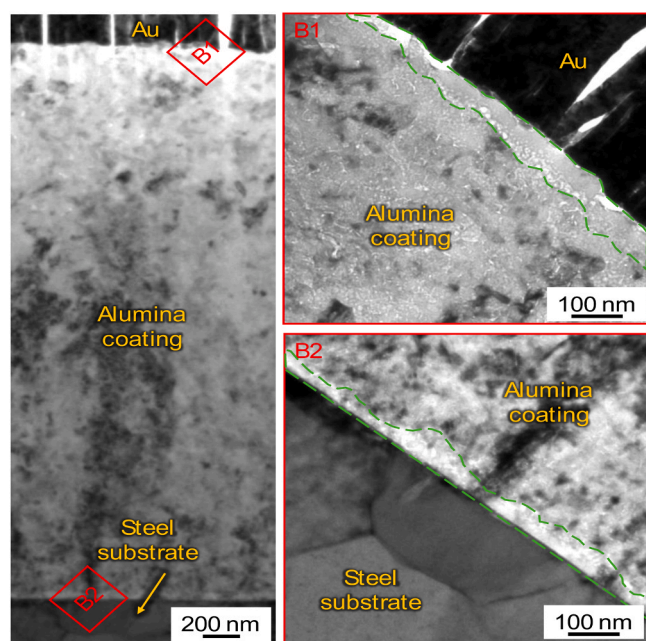


Fig. 3. BF-TEM image of the Al_2O_3 samples after the exposure in Lead-lithium at 550 $^{\circ}\text{C}$ for 7000 hrs; close-up view of the coating outer surface (Box B1) and of the coating-steel interface (Box B2). A dashed green line is used to highlight the formation of distinct phases on the surface and interface after the exposure.

EUROFER97 surface, a distinct feature emerges at the immediate vicinity of the substrate, in which the coating displays a zone of much finer nanocrystals (Fig. 3, Box B2). This interfacial band, not present in the as-deposited samples, suggests a localized crystallization mechanism influenced by diffusion or chemical interactions at elevated temperatures.

The EUROFER97 substrate retains its original martensitic lath structure, with no evident microstructural degradation or corrosion features, confirming the protective efficacy of the Al_2O_3 coating during long-term exposure.

SAED patterns were collected at different regions of the coating, including the surface, the bulk, and the interface with the steel substrate (Fig. 4a–c). After exposure, crystalline diffraction spots appear in all regions, accompanied at the surface by discrete spots, indicative of larger and well-oriented nanocrystals. Spots are arranged in rings, where differently oriented crystals diffract with planes of similar spacings, and the radius of the ring is inversely proportional to the plane spacing. Towards the outer surface of the coating, there are fewer spots and fewer diffracting objects present in the selected area, indicative of larger crystals. Towards the middle, or bulk of the coating, the rings show more spots, reflecting a finer polycrystalline structure composed of smaller, more randomly oriented crystallites. Some spots show smearing around the ring, indicating families of crystals with similar orientations. Moreover, radial broadening of the diffraction rings is observed, which can be associated with local strain or structural disorder. At the steel interface, the rings are sharper and more structured, and an additional low-angle reflection at approximately 2 nm^{-1} appears, suggesting locally enhanced crystallization influenced by the substrate (Fig. 4d).

In parallel, GI-XRD patterns were acquired. To directly compare the crystalline phases identified by a local high-resolution technique (SAED) with those detected by a volumetric diffraction method (GI-XRD), both datasets were converted into one-dimensional intensity profiles in reciprocal space. This approach can eliminate differences arising from the experimental geometry and allows the diffraction features to be compared on the same physical basis. On the 7000 hrs exposed sample (Fig. 4e), well-defined diffraction peaks are observed, confirming the crystallization and the structural evolution compared to the amorphous as-deposited coating.

Main diffraction contributions are evidenced at 19.6, 31.9, 37.7, 39.5, 45.9, 60.7, and 66.9 $2\text{-}\theta$ angles (corresponding to 2.21, 3.57, 4.074, 4.25, 4.90, 6.36 and 6.93 $1/\text{nm}$ in the reciprocal space). These diffraction peaks are characteristic of a spinel structure as in the case of $\gamma\text{-Al}_2\text{O}_3$, the first crystalline phase that is encountered when enough thermal energy is provided to amorphous alumina [40]. Nevertheless, the crystallization of this compound is typically found at higher temperatures. For this reason, other crystalline compounds were considered. Looking at the lithiated alumina phases, LiAlO_2 is characterized by a cubic spinel structure with nearly identical lattice parameters to $\gamma\text{-Al}_2\text{O}_3$ (7.92 $\text{\AA}$ vs 7.9 $\text{\AA}$) and density (3.75 vs 3.55 g/cm^3) [41–44]. In this case,

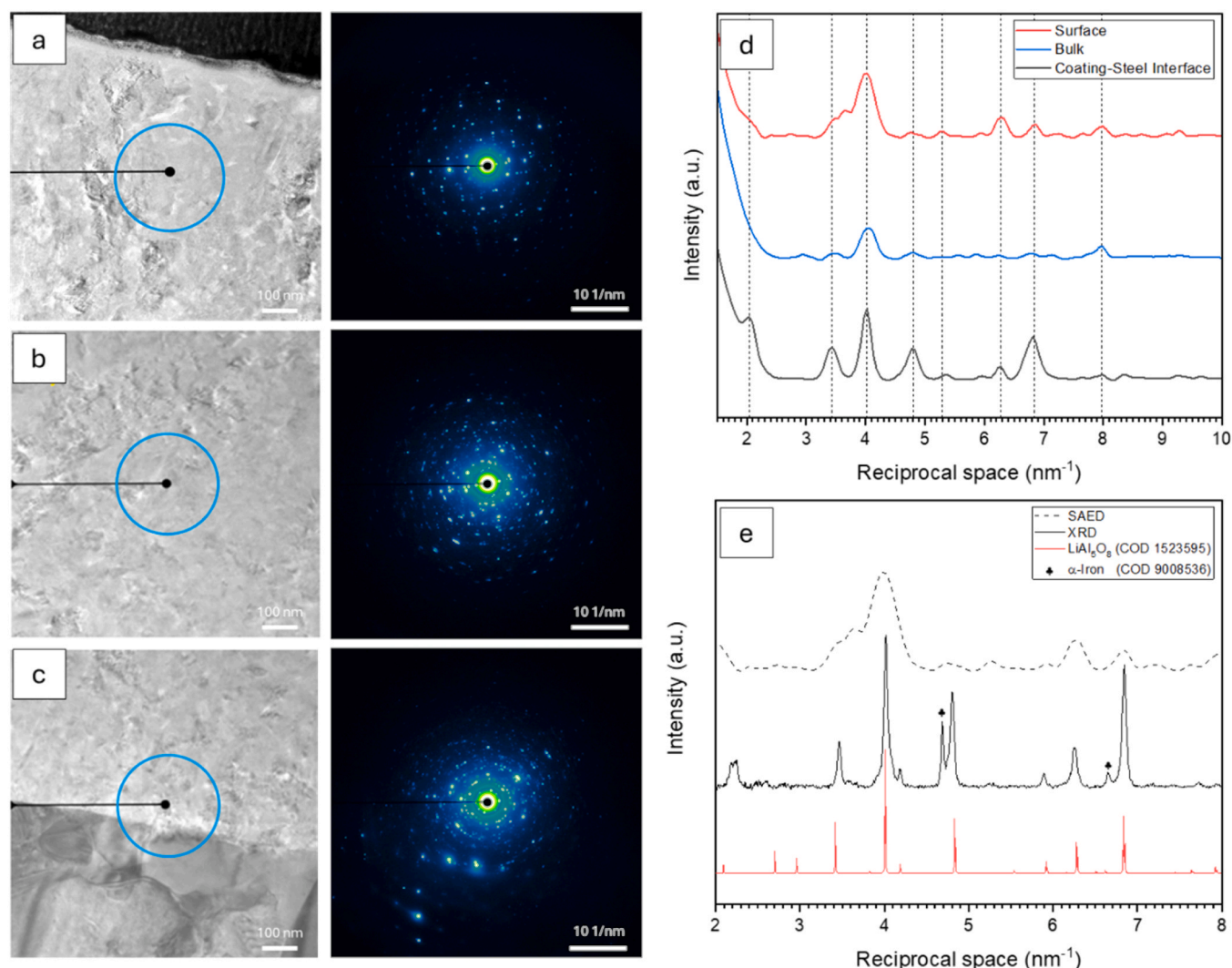


Fig. 4. TEM images and SAED patterns on the surface of the coating (a), in the bulk (b) and close to the steel interface (c) with accompanying rotational average plots (d). A comparison between the SAED profile, the experimental XRD profile and the expected XRD pattern of LiAl₅O₈ converted via Bragg's law (e).

the presence of this compound in crystalline form is more plausible, since the crystallization temperature of LiAl₅O₈ has been experimentally measured in the range 250–300°C [45]. The formation of a lithiated compound is thermodynamically favored under the experimental conditions [46], even if it was associated with the LiAlO₂ in previous studies. However, this phase crystallizes in a rhombohedral structure and its presence can be in the present case neglected due to the absence of diffraction peaks associated with this crystalline group [47]. As a result, after the high-temperature exposure, LiAl₅O₈ can be identified as the predominant crystalline phase. This assumption alone is not sufficient to imply with certainty the presence of a lithiated phase, but it was considered as a first indication that lithium incorporation during high-temperature exposure could have occurred.

SAED patterns were converted into one-dimensional reciprocal-space intensity profiles (Fig. 4d), using the rotational average integration function present in DiffTools™, the electron diffraction software tool for DigitalMicrograph™ [48]. At the same time, XRD diffraction patterns were converted into reciprocal space exploiting Bragg's law [49], and directly compared with SAED-derived profiles. The patterns acquired with the different techniques show excellent agreement, confirming that the same spinel-type crystalline phase forms throughout (Fig. 4e).

Overall, the evolution from the broad amorphous halo in the as-deposited coating to the well-defined diffraction rings and peaks after

lead-lithium exposure demonstrates a clear crystallization pathway, with subtle variations in crystallite size and orientation across the coating thickness.

STEM-EDX elemental maps (Fig. 5) show a less homogeneous chemical distribution than in the as-deposited condition. Local Al-rich and O-deficient areas appear throughout the coating thickness. No foreign metallic species originating from the lead-lithium environment were detected within the coating. Chemical modifications are also observed at the coating-substrate interface. The continuous MnO interfacial layer present in the as-deposited state is no longer detectable after exposure. Instead, discrete Mn-rich nanoparticles are dispersed along the interface region (Fig. 5e). This suggests a redistribution or partial dissolution of the original interfacial oxides under prolonged contact with the liquid metal. The underlying Cr/V-rich passive layer is still visible but appears discontinuous (Fig. 5f-g). M₂₃C₆, VN and TaC precipitates were also detected. 100–200 nm sized AlN grains and 10–15 nm thick V enrichment were found at the interface.

The detailed lithium concentration profile has been measured through XPS. The coating surface was initially sputtered for 30 s to remove most adventitious contamination. Consequently, as described in the experimental section, an alternated sequence of acquisition was followed by Ar + sputtering. This procedure enabled XPS signals to be obtained across the entire coating with high depth resolution, i.e., along the direction perpendicular to the sample surface, minimizing overlap

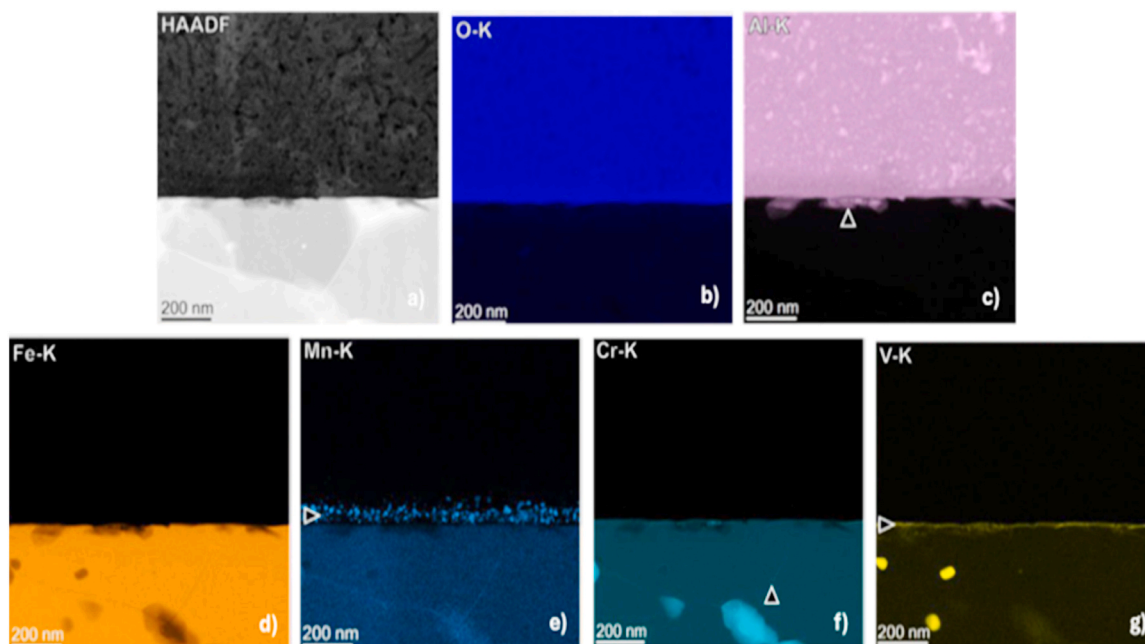


Fig. 5. STEM/EDX elemental maps (O, Al, Fe, Mn, Cr, V) of as deposited 3 μm thick PLD deposited Al_2O_3 coating on EUROFER97.

between the analyzed regions. Al 2 s, Al 2p, O 1 s, Li 1 s, C 1 s, Pb 4 f, and Fe 2p spectra were acquired (reference XPS peaks' positions were taken from the NIST XPS Database [50]). To extract the depth of analysis, the sputtering time was converted knowing the thickness of the coating and the sputtering time required to reach the Fe signal, which identifies that the steel substrate was reached. An overall sputtering time of 40,000 s was required, resulting in a sputtering rate of 0.7–0.8 $\text{\AA}/\text{s}$.

The analysis of the sample exposed for 7000 hrs is reported in Fig. 6. Within the first tens of nanometers, the presence of adventitious carbon and lead contamination affects the chemical environment at the surface.

Carbon and lead impurities are found up to 75 nm in depth; beyond this point, only the Li 1 s, O 1 s, and Al 2p peaks were significantly detected in the XPS analysis, and it can be considered as the end of the altered superficial layer. The O 1 s peak exhibits a contribution consistent with the spectral features typically reported for amorphous alumina [51] [52]. For the Al 2p and Li 1 s peaks, only one component was evident. At approximately 125 nm in depth, the peak features for oxygen and lithium atoms are identical to the previous case. However, Al 2p clearly exhibits the emergence of an additional component at lower binding energies, which can be attributed to metallic aluminum. This

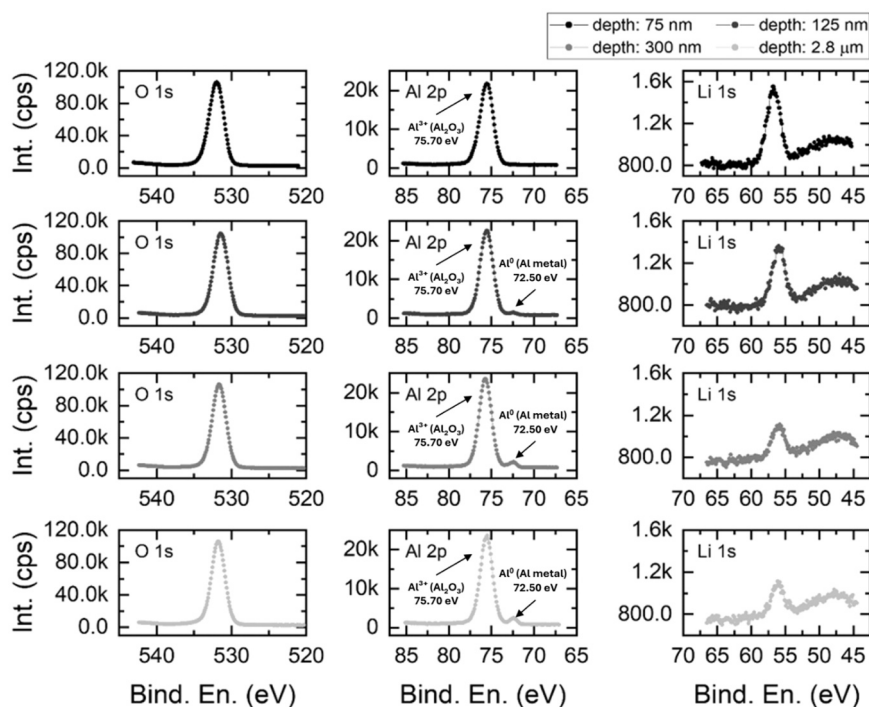


Fig. 6. O 1 s, Al 2p and Li 1 s XPS signals recorded at 75 nm (surface), 125 nm (near surface), 300 nm (bulk coating), and 2800 nm (coating-steel interface) in depth of the sample exposed in Lead-lithium at 550°C for 7000 hrs.

observation suggests partial reduction of aluminum atoms, indicating lithiation processes [29]. After reaching a depth of 300 nm, no significant changes were detected compared to the previous case, and the Al 2p peaks still exhibit the characteristics of metallic aluminum. The XPS spectra remained stable until the appearance of the Fe 2p peak, indicating that the steel substrate was reached.

The same procedure was performed on the samples exposed for 1000 hrs and 4000 hrs to get the effect of the exposure time on the lithium concentration profile. From the analysis of the XPS peaks, no major differences were observed in the behaviour, and the quantitative analysis was afterwards performed with the built-in quantification tool of the CasaXPS software [53]. Results are presented in Fig. 7. In the sample exposed for 1000 hrs it is observed that the Li concentration is 15 at% on the surface and this value steeply decreases to 3–4 at% in a transitory region 50 nm thick and then remains constant in the rest of the coating. The sample exposed for 4000 hrs is characterized by a lithium concentration profile like the previous one. The lithium concentration marks identical values in the superficial region and in the bulk coating while the only relevant difference is the extension of the transitory region that now embraces the first 100 nm in depth. In the sample exposed for 7000 hrs the extension of the transitory region is 200 nm, and it is also possible to recognize that the Li content in this superficial region is constant at 10 at%. Through a direct comparison of the first 500 nm in depth of the coating the different extension of the Li-rich outer region, and so the effect of the exposure time, can be better appreciated.

As discussed above, the XPS analysis can reliably resolve the coating composition only up to the onset of the Fe signal from the underlying EUROFER97 substrate. For this reason, APT was employed to quantitatively assess the elemental distribution with higher spatial resolution, with particular emphasis on the coating–substrate interfacial region. Atom probe volumes were taken from three distinct positions with respect to the coating depth, as described above in the methods section. APT analyses were performed on the two samples exposed for 7000 h, from which a total of five atom-probe needles were prepared. The needles were grouped into two series, referred to as series A and series B, according to their position and orientation with respect to the coating–substrate interface. Their locations and orientations, as well as the concentration of the Al, O and Li elements in the analyzed volumes are schematically indicated in Fig. 8. Overall, five APT volumes were selected at progressively increasing depths, starting from the outer coating surface and moving towards the EUROFER97 substrate, with the deepest volumes extending across the coating–substrate interface and

into the steel substrate. This sampling strategy was adopted to investigate the evolution of the elemental distribution through the coating and in the steel (sample nomenclature is also clarified in [Supplementary Material](#), paragraph S1).

The results show that at the external surface, the Li concentration is 10 at% and as depth increases the Li concentration decreases to 2–3 at% at a depth of 500 nm. Nevertheless, a further increase in lithium concentration can be found in the needles extracted right next to the steel substrate. In this region, lithium is heterogeneously distributed in agglomerates that can contain up to 30–35 at%, giving an average of 7–8 at% in the atom probe volume (roughly $50 \times 50 \times 50 \text{ nm}^3$). This is consistent with a previous study which focused on this interface layer [32]. Moreover, in the volume analyzed in the steel substrate close to the steel-coating interface, no lithium was found.

This demonstrates the high accuracy of APT in measuring the lithium content in all regions of interest.

The identification of these lithium-rich agglomerates, together with the presence of manganese dispersions, as previously demonstrated by EDX measurements, provides an important indication that lithium-manganese oxide species may have formed. Indeed, lithium aluminates cannot reach lithium concentrations higher than 25 at%, whereas manganese can accommodate higher concentrations. Combining SAED diffraction patterns and APT lithium concentration maps acquired in the interfacial region, the presence of Li_2MnO_3 explains both microstructural and chemical analysis results (Fig. 9).

Complementary lithium analyses performed by ion beam techniques and ToF-SIMS are reported in the [Supplementary Material](#).

4. Discussion

4.1. Summary of experimental evidence

During the high-temperature static exposure in molten Lead-lithium, the coating played a key role in the corrosion protection of the EUROFER97 steel substrate beneath. From SEM and TEM micrographs, it was evidenced that the coating has maintained its integrity, though some transformation is indicated. Macroscopically, neither cracked nor delaminated regions were found after up to 7000 hrs of exposure. At the coating-steel interface, no significant microstructural or chemical modification has been detected. These results indicate that the steel substrate was efficiently isolated from the eutectic alloy for the whole duration of the test, consequently preventing heavy liquid metal (HLM) corrosion dissolution attacks.

Nevertheless, it has been demonstrated that the coating was subjected to a progressive microstructural and chemical modification in various regions. This process leads to the formation of interfacial layers with a distinct microstructure and microcrystalline domains dispersed in the rest of the coating.

The formation of ternary compounds has been evidenced in previous Lead-lithium exposures, but in the present work, the lithiated alumina is characterized by a LiAl_5O_8 stoichiometry rather than LiAlO_2 .

From the microstructural point of view, the observation of widespread crystallization at 550°C contrasts with previous investigations of PLD-deposited Al_2O_3 coatings exposed to the same temperature for extended periods. The crystallization kinetics of $\gamma\text{-Al}_2\text{O}_3$ in these systems is strongly temperature-dependent, with crystallization onset occurring above approximately 650°C (complete crystallization have been evidenced at 700°C within 20 h [24]). Prior literature demonstrated that amorphous Al_2O_3 coatings remain amorphous after prolonged heating at 550°C in HLM corrosion tests with lead alone [20]. The presence of crystalline phases throughout the entire coating thickness in the present work therefore highlights the role of lithium in the surrounding environment, whose incorporation is presumed to promote the crystallization of the ternary compound rather than the formation of thermally activated $\gamma\text{-Al}_2\text{O}_3$. This conclusion is further supported by thermal studies of LiAl_5O_8 , which reported the onset of crystallization at

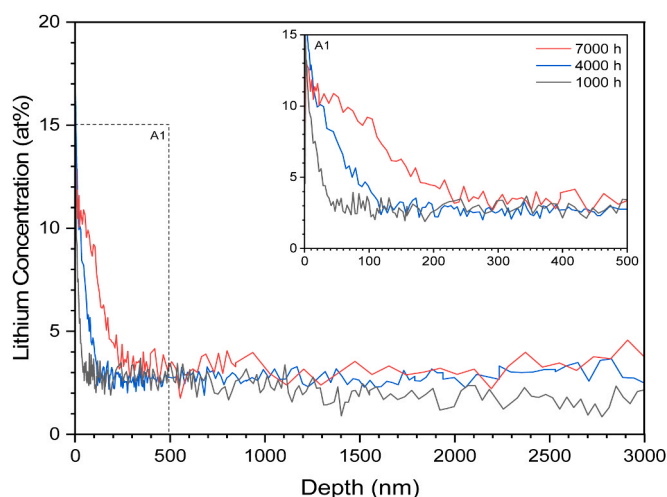


Fig. 7. Lithium concentration profile across the entire coating thickness as a function of the exposure time. The inset in the upper-right corner (A1) shows a magnified view of the first 500 nm of the coating thickness, highlighting the progression of the lithium-enriched front.

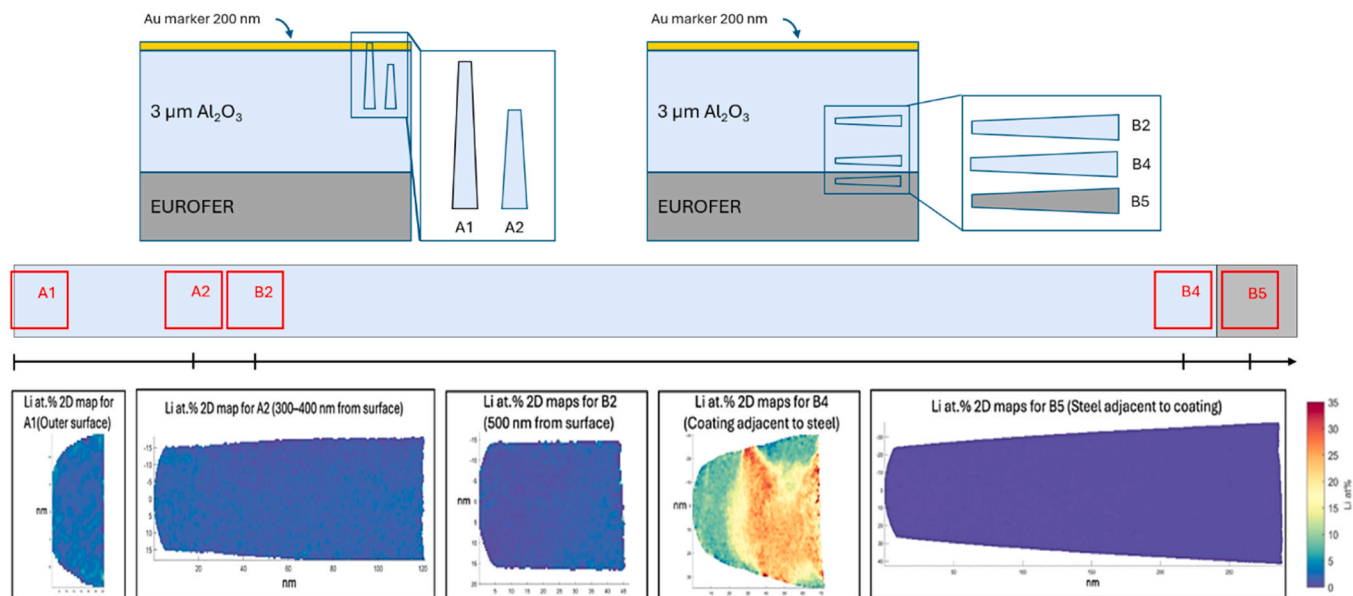


Fig. 8. Results of the elemental analysis by APT of the 3 μm PLD- Al_2O_3 sample after 7000 hrs exposure to Lead-lithium. Results concerning volumes close to the surface (a), in the bulk coating and close to the steel substrate (b).

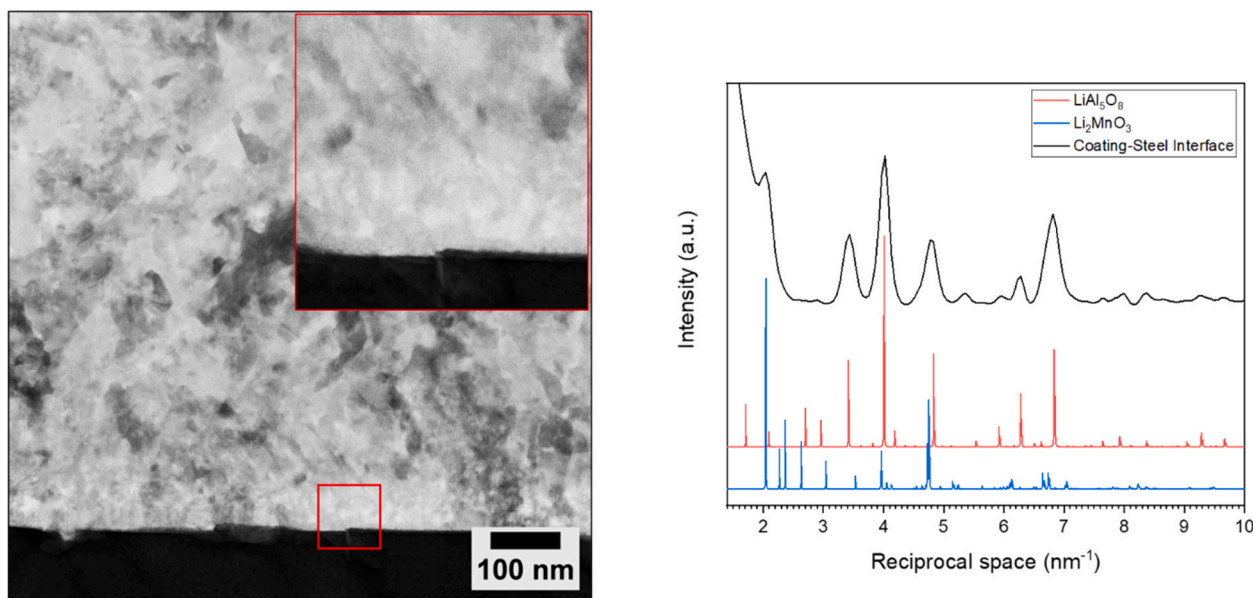


Fig. 9. TEM BF images acquired at the coating-steel interfacial region of the Al_2O_3 -coated EUROFER97 sample exposed for 7000 hrs in lead-lithium, with focus on the finer-grain microstructural features present in the very first tens of nanometers within the coating (left). SAED diffraction pattern and converted XRD diffraction patterns used for crystalline phase recognition.

significantly between 300–400 $^{\circ}\text{C}$ (see [Supplementary Material](#), paragraph S2, [Figure S2c](#)).

It follows that, even if the coating maintains structural integrity, the presence of crystalline phases could worsen the functional performance. This is especially impacting for the capability to block tritium permeation, as the porosities generated as a consequence of the crystallization-induced densification from the amorphous state would offer less resistance to diffusing hydrogen species.

Various elemental analysis techniques highlighted that most of the ceramic coating exhibits a homogeneous composition with aluminum, oxygen, and lithium as the main constituents. It was concluded that Pb and contaminants cannot penetrate from the eutectic alloy through the coating material. Similarly, no interdiffusion or migration of alloying elements from the steel substrate has been detected at the coating-

substrate interface. The combination of sputtering-assisted XPS and APT revealed traces of lithium in different amounts and arrangements throughout the coating. This combination of techniques resulted in the acquisition of a nanoscale-resolved lithium concentration profile.

The reliability of the XPS depth profiles was assessed through dedicated calibration experiments using multilayer reference samples representative of the main coating compositions ($\text{Li-Al-O/Al}_2\text{O}_3$). The resulting sputtering rate was calibrated to 0.6 $\text{\AA s}^{-1}$ and validated across the $\text{Li-Al-O/Al}_2\text{O}_3$ interface. Detailed information on the reference samples, their thickness characterization, and the corresponding XPS depth profiles is provided in the [Supplementary Material](#) (Section S3, [Figures S3-S4](#)). The bulk Li concentration obtained by XPS was further independently corroborated by APT analysis.

This analysis showed that, after the exposure, the Al_2O_3 coating is

divided into three main regions, each characterized by a distinct lithium distribution. A Li-rich topmost layer at 10–15 at% on the outer surface (up to 200 nm) is followed by a flat lithium concentration profile at 3–4 at%. At the coating-steel interface (50–100 nm), a thin layer characterized by localized aggregation, reaching 30–35 at% concentration of lithium.

The extent of these regions matches the features' dimension highlighted by TEM cross-sectional images, suggesting that the difference in lithium content is also accompanied by a difference in microstructural organization.

The topmost layer is identified as crystalline LiAl_5O_8 . A slightly higher lithium content than the stoichiometric composition (7.14 at%) can be readily attributed to the presence of lithium-rich lithium aluminate LiAlO_2 in small inclusions or to surface contamination by LiCO_3 or LiOH , which are typically formed in contact with the outer atmosphere.

The bulk coating region is characterized by nanocrystalline domains and voids heterogeneously dispersed. Despite this disordered microstructure, the lithium distribution in this part of the samples was found to be homogenous and independent from the exposure time. This parameter only affects the thickness of the Li-rich superficial layer, which remains in any case extremely confined to the outer surface even up to 7000 h.

APT was effective on elucidating the lithium concentration at the steel-coating interface and in the substrate, showing the presence of agglomerates with up to 30–35 at% of lithium remarkably close to the interface, and with limited diffusion of lithium into the steel. The nanocrystalline structure at the interface was found to have a high concentration of lithium by APT, but TEM-EDS and APT disagreed on the presence of manganese. This may be because the samples were taken from different exposed samples. However, it seems this lithium-enriched nanocrystalline layer forms with and without the presence of manganese.

4.2. Lithium incorporation and bulk diffusion

Lithium incorporation into amorphous Al_2O_3 may involve both chemical reduction of the oxide and ionic transport of Li-containing species. In particular, Li^+ diffusion through Al_2O_3 has been investigated in the context of lithium-containing oxide materials, and its mobility depends strongly on the structural and chemical state of the oxide [54].

Lithium in the metallic state cannot directly incorporate into an amorphous ceramic, as the covalent network does not provide energetically favorable sites to accommodate them (its incorporation would require the preservation of a neutral metallic state in a strongly oxidizing environment, which is not favorable neither as interstitial nor as substitutional atoms) [54]. Instead, lithium readily undergoes oxidation to Li^+ , which can be embedded in an amorphous Al_2O_3 ceramic matrix through the partial reduction of Al^{3+} ions, thereby preserving the local charge neutrality [54,55]. When inserted in the amorphous ceramic, Li^+ ions typically possess high mobility, and their transport within the coating material can be controlled by the application of an electrical potential [56]. These assumptions have been widely used in the field of solid-state electrolytes for lithium-ion batteries and will be considered here.

However, it has also been showed that lithium transport in Al_2O_3 depends on the structural and chemical state of the oxide, with Al-deficient and structurally disordered configurations that could provide favorable pathways for lithium migration also in the case of low oxygen activities in the lithium-containing medium [54]. This is particularly relevant to the present system, where XPS indicates partial reduction of Al in the exposed coating. Thus, ionic transport may contribute to Li redistribution after the initial chemical modification of the alumina, rather than necessarily representing the primary mechanism by which Li first enters the pristine oxide.

Therefore, the diffusion model adopted here should be regarded as a phenomenological description of Li redistribution within the coating

rather than as proof of a specific microscopic transport mechanism.

In the present work, lithium transport within the ceramic coating is analyzed by considering diffusion in the amorphous Al_2O_3 matrix after lithium is incorporated at the coating surface. The overall transfer of lithium from the lead-lithium eutectic into the ceramic is therefore conceptually separated into interfacial transfer and bulk diffusion. The diffusion model presented in the following is intentionally restricted to the latter process and is used to interpret the experimentally measured lithium concentration profiles under a diffusion-limited approximation.

Following the “electrolyte model” [57], the amorphous ceramic coating is treated as a conventional liquid electrolyte, where a mobile ionic species (in this case Li^+ cations) is free to move while compensated by a constant immobile distribution of ions with opposite charge (in this case O^{2-}). It was assumed that during lithium insertion, the Al:O stoichiometric ratio remains constant and the volume expansion can be neglected [57]. The lower-binding-energy contribution observed in the Al 2p XPS spectra is consistent with partial reduction of Al species in the bulk coating. This observation does not, by itself, distinguish whether the reduction occurs through direct reaction with metallic Li or through an electrochemical/ionic pathway involving Li^+ . However, it provides evidence that Li incorporation is accompanied by a significant chemical modification of the alumina matrix.

For modelling purposes, the lithium atomic fraction in the eutectic cannot be used directly, as lithium exists in a metallic state in the liquid alloy and as a mobile ionic species in the ceramic matrix. To ensure a physically consistent description, the lithium content of the eutectic was therefore converted into a volumetric concentration, which was adopted as the surface boundary condition for lithium diffusion into the coating.

Assuming the nominal eutectic composition (15.7 at% Li), a density of $\rho \approx 9.54 \text{ g/cm}^3$ at 550°C , and a molar mass $\text{MM}_{\text{Pb-Li}} = 175.76 \text{ g/mol}$, the resulting lithium volumetric concentration is $C_{\text{Li, eutectic}} \approx 5 \times 10^{21} \text{ at/cm}^3$.

The amorphous Al_2O_3 coating was treated as a homogeneous diffusion medium. Using a measured density of 3.6 g/cm^3 , the density of Al_2O_3 units is approximately $2 \times 10^{22} \text{ atoms/cm}^3$, corresponding to $\sim 4 \times 10^{22} \text{ Al atoms/cm}^3$ and $\sim 6 \times 10^{22} \text{ O atoms/cm}^3$. Within this diffusion-limited approximation, lithium uptake in the amorphous Al_2O_3 proceeds until a steady-state lithium concentration is established in the coating, which is governed by the lithium availability at the interface and by the diffusion kinetics in the ceramic, rather than by the intrinsic solubility limit of the oxide.

The experimentally measured lithium content in the bulk of the coating (3–4 at% corresponds to $3\text{--}4 \times 10^{21} \text{ atoms/cm}^3$) approaches the simulated value ($5 \times 10^{21} \text{ at/cm}^3$), and remains constant with increasing exposure time, indicating that a steady-state concentration has been established and suggesting that a saturation limit was reached. Although higher lithium contents could in principle be accommodated in amorphous alumina, the maximum concentration reached in the present system is limited by lithium availability in the eutectic.

From a mechanistic perspective, the rapid bulk Li uptake should therefore not be interpreted as evidence for a purely ionic diffusion process. The calculated diffusion timescale is substantially shorter than the minimum experimental exposure time, and the bulk Li concentration reaches a stable value of approximately 3–4 at% within 1000 h and remains essentially unchanged after 7000 h. The simultaneous detection of reduced Al species throughout the coating is consistent with a reduction-dominated modification of the alumina matrix. Once such chemical and structural modifications occur, ionic transport of Li-containing species may contribute to subsequent redistribution within the coating.

4.3. The Kinetics of Lithium Thermal Diffusion

The kinetics of diffusion were simulated to evaluate the time scale of the lithium intercalation process in the initially amorphous ceramic. Even if the corrosion experiment was conducted under static conditions,

the Li concentration in the eutectic was considered constant, since the volume of the molten alloy is much larger than the volume of the coating, so that lithium uptake by the ceramic does not measurably alter the lithium concentration in the eutectic during the experiment. Thanks to this assumption, the eutectic can be treated as an effective lithium reservoir, allowing the adoption of a constant surface concentration boundary condition and the use of a simplified solution of the Second Fick's Law [58]:

$$C(x,t) = C_s + (C_0 - C_s) \cdot \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

where $C(x,t)$ is the concentration of the diffusive species as a function of the depth in the coating (x) and the time (t), C_0 is the initial concentration of the species in the coating, C_s is the constant concentration of the species on the surface of the coating, and D is the diffusion coefficient. The initial concentration C_0 was set equal to zero, while the constant surface lithium concentration was set equal to the lithium volumetric concentration in the eutectic.

Considering the pre-exponential factor and the activation energy for the lithium diffusion process in amorphous Al_2O_3 from literature [56], following an Arrhenius-type dependence ($D(T) = D_0 \cdot \exp(-E_{\text{eff}}/(k_B T))$), the diffusion coefficient at 550 °C was estimated as $D_{\text{Li}}(550^\circ\text{C}) = 3.70 \times 10^{-9} \text{ cm}^2/\text{s}$.

Model calculations indicate that a diffusion-controlled steady-state lithium concentration is reached within a few hours (Fig. 10), well below the minimum experimental exposure time, explaining the weak time dependence observed in the bulk lithium profiles.

Once the diffusion-controlled steady state is achieved, further lithium accumulation near the outer surface and at the coating–steel interface cannot be described by a single bulk diffusion process with constant boundary conditions.

These regions exhibit slower kinetics and higher lithium content, likely associated with local lithium accumulation mechanisms, such as oxygen-driven formation of lithium-rich surface species that can function as secondary lithium reservoirs at the coating surface. Under static conditions, lithium oxide particles formed in the melt may function as a persistent lithium reservoir at the coating surface, promoting the development of a compact lithium aluminate scale.

Diffraction analyses reveal the formation of LiAl_5O_8 crystalline domains, consistent with the experimentally measured lithium concentration. However, the stoichiometric lithium requirement of LiAl_5O_8 cannot be fulfilled throughout the entire coating within the diffusion-limited approximation adopted in this model, explaining the coexistence of crystalline regions with lithium-poor or amorphous domains in the bulk. Lithium mobility in the stoichiometric phase is reduced, which rationalizes the slow growth kinetics of the surface scale.

Overall, lithium uptake in amorphous Al_2O_3 is governed by a fast initial diffusion process leading to a diffusion-controlled bulk steady state, followed by slower, interface-controlled mechanisms that drive local lithium enrichment and crystallization. These findings highlight the limitations of purely diffusive models and motivate the inclusion of thermodynamic considerations to fully describe the evolution of the coating under Pb–Li exposure.

4.4. Thermodynamic stability of oxide ceramics in Pb–17Li

Early thermodynamic assessments identified oxide ceramics as the most promising candidates for application in Pb–Li environments [46]. Al_2O_3 was predicted to exhibit good thermodynamic stability and was therefore proposed as a reference ceramic material. However, these evaluations were conducted under boundary conditions that were not fully representative of the actual operating environment.

Specifically, earlier calculations did not systematically account for the influence of key thermodynamic parameters such as the lithium activity, the activity of metallic species dissolved in the eutectic (often assumed to be unity), and the activity of non-metallic solutes. Most studies considered either oxygen-saturated lead-lithium or cold-trapped lithium, limiting the applicability of their conclusions to real operating conditions, where activities and impurity levels may deviate significantly from these idealized cases [59].

The thermodynamic treatment of ternary Li-containing compounds is challenging because consistent thermodynamic data for these phases are still limited, while their formation may additionally involve different reaction pathways, phase equilibria, and local activity conditions compared with binary oxide formation.

Considering the present experimental evidence, a more comprehensive thermodynamic analysis was therefore required. New calculations were performed explicitly incorporating the effects of lithium activity, dissolved metallic species, and non-metallic impurities.

From a thermodynamic standpoint, lithium transfer to a binary oxide is governed by the lithium activity in lead-lithium, which is significantly lower than unity and strongly temperature dependent. In scenarios involving lithium incorporation or the formation of ternary Al–Li–O compounds, additional contributions from aluminum and from dissolved oxygen, nitrogen, and hydrogen in the liquid metal must be considered. While pure lithium readily reacts to form Li_2O , Li_3N , or LiH upon contact with the corresponding non-metals, its reduced chemical activity in eutectic alloys alters the driving force for these reactions.

Predominance diagrams were employed to identify the ranges of chemical potential (or effective partial pressure) over which specific compounds are thermodynamically stable. Oxygen and nitrogen were considered the most relevant impurities, and the stability of Li_2O and

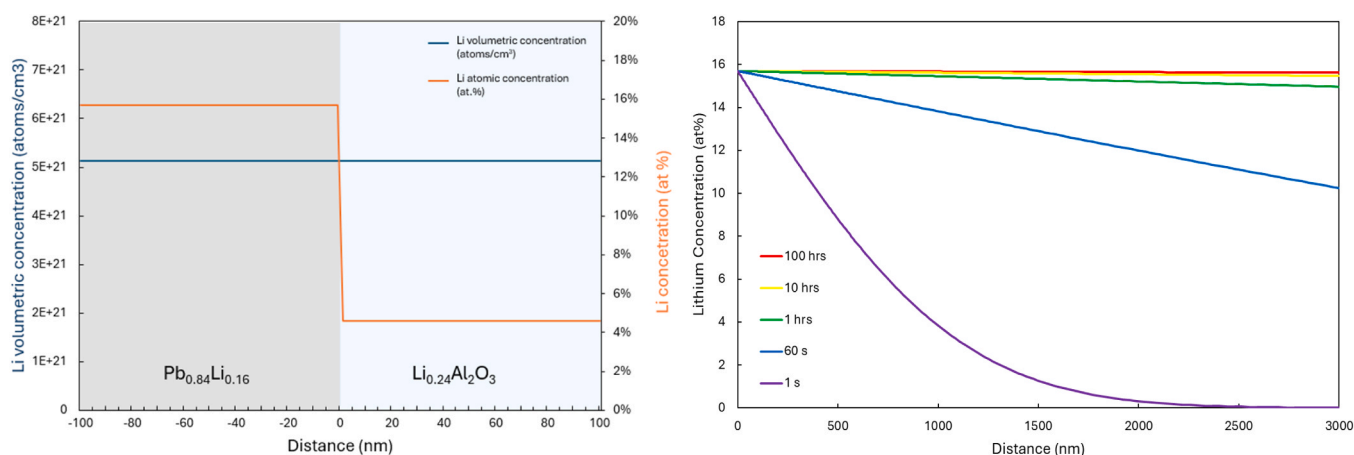
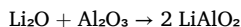
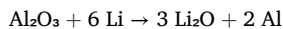


Fig. 10. Graphical representation of the saturation condition. (left) Lithium volumetric concentration in Pb–Li and atomic concentration in the alumina coating. (right) Lithium concentration profiles in amorphous alumina, normalized to the saturation concentration.

Li_3N was evaluated accordingly. The calculations were based on thermodynamic data for binary Al_2O_3 and ternary Al–Li oxides such as LiAlO_2 [60][61] using the HSC Chemistry® database (Version 5.0) [62] (While data for LiAlO_2 were accessible, calculations for LiAl_2O_3 were not possible due to the lack of thermodynamic entries).

The traditional reaction pathway involves a two-stage mechanism:

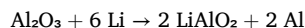


In this case, an oxygen-mediated pathway involving oxidized Li species remains possible. To verify if this species can be effectively present in the liquid metal, stability charts were computed as a function of oxygen and nitrogen partial pressures (Fig. 11a). Calculations were made under the assumption of a unitary activity of aluminum in the melt ($a_{\text{Al}} = 1$), corresponding to an Al-saturated liquid Pb–17Li phase. This represents the reference condition from which the effect of decreasing Al activity on the relative stability of Al-containing phases is evaluated.

It is noted that in eutectic lead-lithium at 550 °C Li_3N formation is unlikely, whereas the stability field of Li_2O can be reached. This

evidence highlights the importance of proper oxygen control, as impurities in the form of lithium oxide could affect the interaction framework and the results in static corrosion tests. Unfortunately, direct determination of dissolved oxygen in molten Pb–Li remains experimentally challenging [64]. Oxygen-controlled corrosion experiments in molten Pb have demonstrated that very low oxygen concentrations can be maintained under controlled conditions (10^{-6} – 10^{-8} wt% [7,20]). In any case, these studies confirm both the relevance of oxygen activity to HLM/ceramic interactions and therefore, without the actual measure of the oxygen content, an oxygen-mediated oxidation of Li and subsequent Li^+ transport cannot be completely excluded in the present study.

However, an alternative direct mechanism was also proposed in literature, which does not involve the presence of Li_2O , but suggested that the reaction could have been triggered by direct aluminum reduction [65]:



Considering such a scenario, results reported in Fig. 11b indicate that, in any case for aluminum, the ternary lithium aluminate LiAlO_2 is thermodynamically more stable than binary Al_2O_3 over the entire

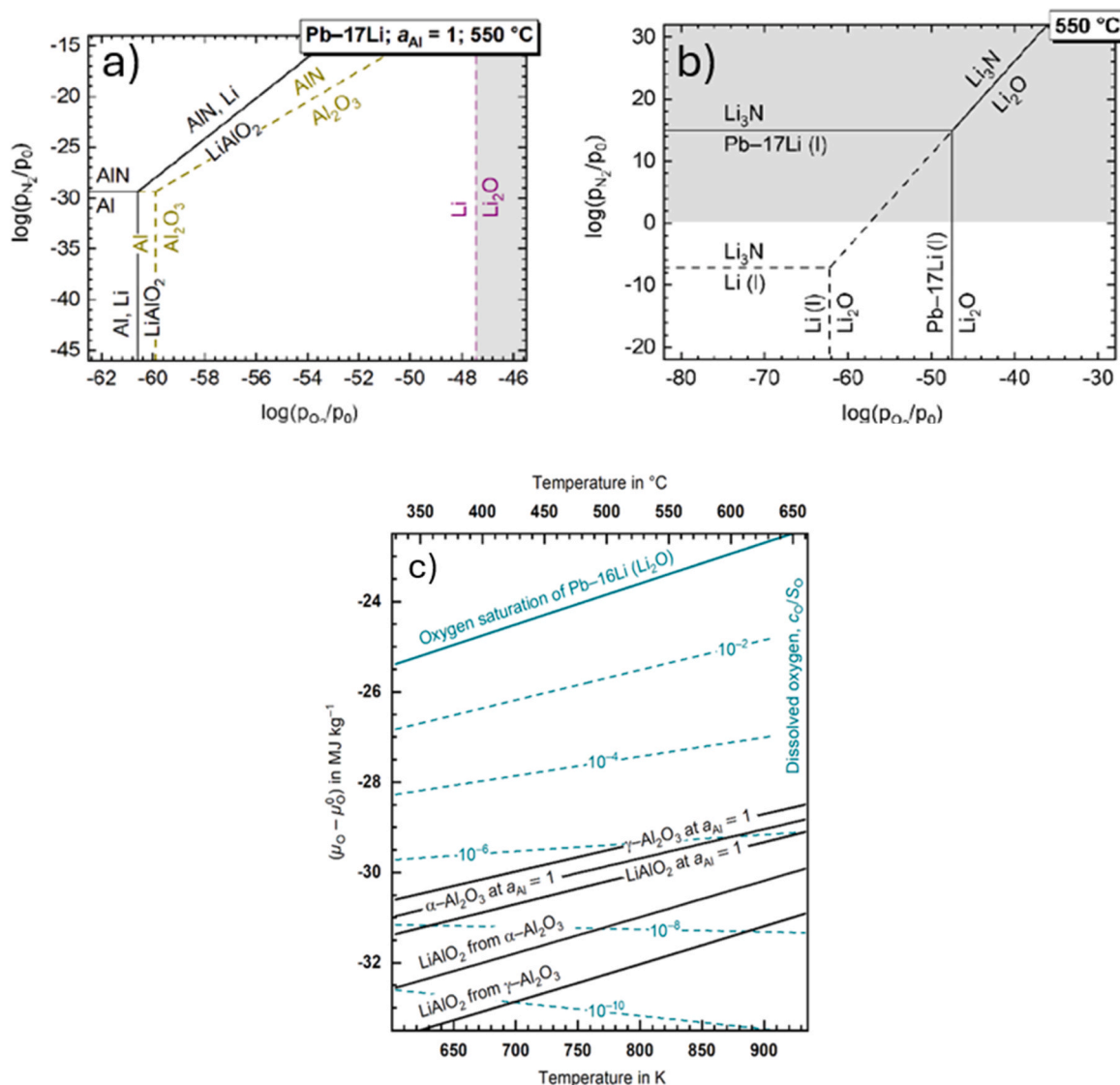


Fig. 11. Oxygen chemical potential in Pb–Li as a function of temperature for varying $c_{\text{O}}/S_{\text{O}}$, i.e., degree of oxygen saturation. Predominance diagram for oxides and nitrides of Al (Pb–Li; $a_{\text{Al}} = 1$; 550 °C) (Left); Predominance of solid Li_2O and Li_3N at 550 °C as a function of the partial pressures of O_2 and N_2 for pure Li and Pb–Li. Ellingham-type diagram of oxygen chemical potential over temperature showing stability lines for Li_2O , α - and γ - Al_2O_3 as well as LiAlO_2 , calculated from the standard free energy of formation of the binary [60] and ternary [61] oxides, for Li activity as in Pb–Li [63].

temperature range considered. It follows that the formation of the ternary compound is expected at reasonable effective oxygen partial pressures attainable and below the threshold for Li_2O formation.

These findings challenge the traditional paradigm used for ceramic selection based solely on Gibbs free energy comparisons and demonstrate that thermodynamic screening must be revisited using updated databases and boundary conditions. Since the ternary oxide is more stable than Al_2O_3 under these conditions, oxygen control alone may be insufficient, and additional mitigation strategies are required.

The present study also underlined the formation of lithiated compounds with lower lithium concentration (LiAl_5O_8) in the bulk and higher lithium concentration at the outer surface. This behavior can be consistent with stoichiometric limitations and local lithium activity gradients. Lithium diffusion from the liquid metal into amorphous Al_2O_3 is driven by lithium activity at the liquid-metal/ceramic interface. The thermodynamic driving force can lead to ternary oxide formation once sufficient local enrichment is reached.

Using standard Gibbs free energies, Ellingham diagrams for crystalline alumina species $\alpha/\gamma\text{-Al}_2\text{O}_3$ and LiAlO_2 (Fig. 11c) indicates that conversion from binary to ternary oxide is favored at low oxygen potentials, consistent with limited oxygen availability in Ar- H_2 cover gas. Amorphous Al_2O_3 , being even less stable than crystalline phases, should be particularly prone to this transformation.

Surface regions in direct contact with the eutectic exhibit higher lithium and oxygen activities, enabling formation of LiAl_5O_8 and locally LiAlO_2 . Lithium transport into the underlying Al_2O_3 continues across the ternary/binary oxide interface but occurs with a higher activation barrier than diffusion in the amorphous matrix, explaining the slower growth of the outer ternary layer.

The last region to address is the coating-steel interface. In this case, alternating Li and Al-rich domains suggest local variations in ion mobility and activity gradients not aligned with the average profile across the thickness. Similar phenomena were observed in ternary-oxide formation during Fe-Cr alloy oxidation [66] and it is reasonable that the presence of manganese in the coating locally altered the chemical potential of oxygen and aluminum, promoting the arrangement of lithium in more stable lithium-rich phase as could be the lithium-manganate oxide form.

4.5. Comprehensive interaction model

All considered, a model is suggested to describe the experimental evidence acquired.

The distinct kinetic regimes suggest that Li incorporation cannot be described by a single homogeneous mechanism throughout the coating. The rapid establishment of the bulk Li concentration is consistent with a reduction-dominated chemical modification followed by rapid redistribution, whereas the progressively developing surface enrichment is more consistent with a slower interface-controlled process involving local Li and oxygen activities and potentially ionic transport of Li-containing species.

By thermal diffusion, Li quickly saturates the amorphous alumina reaching a saturation concentration of 3–4 at% in less than 1000 hrs; in this phase of the lithiation process the limiting factor is the amount of lithium in the eutectic alloy. For this reason, the lithium content in the coating is constant and independent of the exposure time.

Later, thermodynamically stable LiAl_5O_8 crystalline phase is slowly formed at the outer surface of the coating in contact with the molten Lead-lithium eutectic alloy. Two mechanisms are proposed for the formation of this layer:

- 1) Without an accurate control of the oxygen amount in the eutectic, Li_2O can precipitate and be deposited on the surface of the coating effectively constituting a new source of lithium that can interact and diffuse in the ceramic. These particles in static corrosion tests can

easily stick onto the surface of the coating, where it slowly interacts with Al_2O_3 .

- 2) The cover gas effectively removes the oxygen from the eutectic alloy. Under this condition, if the low oxygen activity (a_{O}) drops below a threshold value, the stability of the ternary compound is promoted. This low activity of oxygen in the Lead-lithium melt might explain why LiAl_5O_8 is formed instead of the more common LiAlO_2 phase.

This secondary interaction possesses a slow kinetic, and the lithium-rich region reaches only 200 nm in depth after 7000 hrs of exposure. In the direct contact zone with Lead-lithium (topmost 20 nm) the modified surface layer can locally retain even higher content of lithium (15–17 at %) due to the presence of impurities, grain boundaries, and porosities. An additional enrichment of lithium in the coating has been detected in the region close to the interface with the steel substrate. In this case, even if the activity of lithium and aluminum atoms is low, a new thermodynamic driving force results from an increase in the activity of oxygen, which could be related to the decomposition of less stable manganese oxide impurities in Al_2O_3 .

The lithiation issue described in the present study deserves proper attention and further investigations. It must be considered that this phenomenon does not significantly affect the performance of the barrier in terms of corrosion protection of the steel substrate. Nevertheless, the chemical and microstructural modification of amorphous Al_2O_3 could modify the permeation, electrical insulation, and radiation damage behaviour of the coating.

The reaction between energetic neutrons and lithium atoms embedded in the coating will generate tritium and He atoms, because of $\text{Li}(n,\alpha)\text{T}$ reaction; T and He gases possess high mobility and can migrate easily in the amorphous coating matrix also filling the voids formed during irradiation or build-up trapping sites. In those regions the internal pressure is increasing until it results in microcracks, swelling and rupture of the near-surface layer of the ceramic. This issue has been investigated in fusion-relevant lithiated ceramics to be used as lithium breeders in pebble bed designs, but data on Al_2O_3 are still missing [33, 34,67–71].

This aspect is particularly critical at the coating/steel interface, where lithium accumulation may occur. In such regions, the local enrichment of Li can exacerbate helium and tritium generation under neutron irradiation, increasing the risk of gas trapping, microcrack formation, and localized mechanical degradation. While lithiation should ideally be mitigated through the design of an appropriate thin-film composition, the condition of the steel substrate surface must also be carefully considered prior to coating deposition. Surface preparation and pre-treatment can play a decisive role in limiting Li accumulation and preventing detrimental, localized effects at the interface that could compromise coating performance and long-term reliability.

5. Conclusions

The interaction between amorphous Al_2O_3 coatings and liquid lead-lithium at 550 °C proceeds through distinct kinetic regimes. During the initial exposure period, Li rapidly accumulates throughout the coating and reaches a stable bulk concentration of approximately 3–4 at % within 1000 h. The observed concentration profiles can be quantitatively described by a diffusion model, which predicts equilibration on a timescale much shorter than the experimental exposure times. The model should, however, be regarded as a phenomenological description of Li redistribution rather than as evidence for a specific microscopic transport mechanism.

The simultaneous detection of reduced Al species throughout the coating is consistent with partial reduction of the alumina matrix and supports a reduction-dominated interpretation of bulk Li incorporation. Ionic transport may subsequently contribute to Li redistribution, particularly as reduction-induced chemical and structural modifications can provide more favorable environments for Li migration. At longer

exposure times, the interaction becomes increasingly interface-controlled, leading to the development of a Li-enriched surface layer and crystallization into LiAlO_2 . The markedly different kinetics of the bulk and surface regions indicate that a single transport mechanism cannot fully describe the evolution of the coating.

The available experiments cannot unambiguously discriminate between direct Li-induced reduction and Li^+ -mediated transport. In particular, because dissolved oxygen was not directly measured, an oxygen-mediated contribution to Li oxidation and ionic transport near the coating/eutectic interface cannot be excluded. Nevertheless, the combination of Al^0 formation throughout the coating, rapid bulk Li saturation, the oxygen-controlled nature of comparable HLM experiments, and the distinct kinetics of the surface-enriched region makes a reduction-dominated mechanism in the bulk the most consistent interpretation of the present data.

Despite lithium uptake and partial crystallization, no lithium penetration into the EUROFER97 substrate is observed, confirming the Al_2O_3 coating's barrier function under the investigated conditions. Beyond fusion blanket applications, these results are relevant to a broader class of lithium-containing environments, including liquid-metal batteries, lithium-based thermal energy systems, and ceramic coatings exposed to reactive alkali metals. Importantly, this work highlights the necessity of combining complementary high-resolution techniques, such as XPS depth profiling, atom probe tomography, and electron diffraction, to reliably identify, quantify, and spatially resolve lithium in complex ceramic systems, where single-technique approaches may lead to incomplete or misleading interpretations.

CRediT authorship contribution statement

A. Stinchelli: Writing – original draft, Visualization, Investigation, Formal analysis, Data curation. **B. Paladino:** Writing – review & editing, Visualization, Investigation, Formal analysis, Data curation. **A.J. London:** Writing – review & editing, Visualization, Investigation, Formal analysis, Data curation. **A. Fazi:** Writing – review & editing, Visualization, Investigation, Formal analysis, Data curation. **F. De Boni:** Visualization, Investigation, Data curation. **M. Klimenkov:** Visualization, Investigation. **M.T. Dürschnabel:** Visualization, Investigation. **G. Leonardi:** Writing – review & editing. **J. Julin:** Writing – review & editing, Visualization, Investigation. **A. Priebe:** Writing – review & editing, Visualization, Investigation. **J. Michler:** Writing – review & editing, Supervision, Resources. **M. Laitinen:** Writing – review & editing, Supervision, Resources. **M. Angiolini:** Supervision, Resources, Project administration. **S. Bassini:** Supervision, Resources, Project administration. **M. Prato:** Writing – review & editing, Supervision, Resources, Methodology, Investigation. **C. Schroer:** Writing – review & editing, Visualization, Supervision, Methodology, Investigation. **M. Utili:** Supervision, Resources, Project administration, Funding acquisition, Conceptualization. **M. Thuvander:** Writing – review & editing, Supervision, Resources. **F. Di Fonzo:** Writing – review & editing, Supervision, Resources, Methodology, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Views and opinions expressed are, however, those of the author(s) only and do not necessarily reflect those of the European Union or the European Commission. Neither the European Union nor the European Commission can be held responsible for them.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.corsci.2026.114256](https://doi.org/10.1016/j.corsci.2026.114256).

Data availability

Data will be made available on request.

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