Development of anti-permeation and corrosion barrier coatings for the WCLL breeding blanket of the European DEMO

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ABSTRACT

Tritium permeation from breeder material to the Water Coolant System (WCS) in Water Cooled Lithium Lead (WCLL) Breeding Blanket (BB) is one of the technological issues to be solved in the design of the European DEMO. Since the tritium extraction from the Water Coolant System is more challenging and expensive than the extraction from the eutectic alloy PbLi, it is mandatory to use of a protective coating on the blanket wall to minimize the permeation rate. Moreover, a protective coating can prevent the corrosion of EUROFER steel by the action of PbLi.

alumina-based coatings are considered as reference for barriers thanks to their good chemical compatibility with the PbLi alloy and their capability to reduce permeation. Three coating technologies were selected in the frame of the EUROfusion project: electrochemical ECX (chemical deposition) process, Pulsed Laser Deposition (PLD) and Atomic Layer Deposition (ALD) coating. The coatings were developed and optimized in order to satisfy the design requirements of good mechanical compatibility with steels, strong adhesion, corrosion compatibility in PbLi at relevant BB design conditions and a Permeation Reduction Factor at least of 200 under neutron irradiation. The present paper aims to describe the status of the technologies and the main results obtained.

The final objectives of the R&D activities are to demonstrate the applicability of the coating to WCLL BB and therefore the scale-up of the technologies from laboratory scale to the BB scale.

1. Introduction

In the Water Cooled Lithium Lead (WCLL) Breeder Blanket (BB) the permeation of tritium from the eutectic alloy PbLi, the breeder, to the water coolant system is one of the critical issues to be managed. The possibility to realise a coating on the water pipes, manufactured in EUROFER, at the PbLi interface can mitigate several major risks and improve considerably the WCLL performances. An effective barrier should decrease the permeation of a factor at least of 200, reducing the total inventory of T in the water cooling that at the moment is estimated of around 150 g [1]. The current analyses and calculations are indicating that the use of coating layers (at least at lower performance, a Permeation Reduction Factor higher than 200), will be mandatory for the operation of the WCLL concept in DEMO. The availability of these barriers at higher Permeation Reduction Factor, defined as PRF the ratio of the flux through an uncoated pipe over the flux through a coated one, can largely increase the performances and safety margins of this concept so that the development of this technology is posed at a high level of priority in the R&D plan. A protective coating can act also as anticorrosion barrier, the results about the corrosion behaviour of the EUROFER in PbLi have shown a strong dissolution of the steel by the liquid metal [1]. The corrosion phenomenology is linked to the dissolution of

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alloying elements in PbLi, where the separation of atoms from the solid matrix into the liquid occurs due to the difference between the chemical activity (chemical potential) in the solid and in the liquid of a particular steel component. The corrosion attack is (besides impurity levels) a function of the temperature and the velocity of the PbLi at the interface. In WCLL BB the PbLi corrosion rate is estimated lower than 1.0 μm/yr [2] due to low PbLi velocity and temperature profile at the interface with EUROFER [3]. However, due to the total PbLi and EUROFER interface area, about 40,000 m^2, the total amount of dissolved (and activated) corrosion products in all BBs modules is higher than 100 kg, high enough to create issues to the correct operation of the system [4]. This considerable amount of material can be transported by the PbLi and set down in the coldest parts of the blanket and/or of the PbLi loop, thus causing blockage issues.

The developed coating technology can be applied on EUROFER water pipes and PbLi pipes in order to reduce, not only the tritium permeation and corrosion rate, but also the large pressure drops due to Magneto-Hydro Dynamics (MHD) effects generated by electrically coupling of the steel wall to the PbLi flow under relevant magnetic field. A strong mitigation of the MHD effects could be achieved with a very good insulating coating. In particular, the MHD pressure losses can achieve very high values in the inlet and outlet pipes of the inboard and outboard of the BB segment, where the magnetic field reaches up to 8.64 T together with a PbLi velocity up to 0.5 m/s. This combination generates a total pressure drop of 2.43 MPa in the inboard and 1.609 MPa in the outboard [5]. Indeed, the use of coatings will allow to increase the PbLi velocity in the reactor and to reduce the manifold and pipe diameters. Coating technologies are investigated in the BB programme as potentially able to avoid the three mentioned risks.

2. Coating operation in DEMO reactor

Coatings are passive barriers that can be applied inside the BB modules in order to reduce tritium permeation from the breeder to the coolant and the corrosion rate of the structural material (EUROFER), Fig. 1, and inside PbLi pipes in order to reduce the tritium permeation from the breeder to the environment, the corrosion rate of PbLi pipes and the MHD effects, Fig. 2.

The estimated overall length of the PbLi pipework is about 3.7 km, the PbLi velocity at 280 330 °C inside the pipes is lower than 0.5 m/s requiring 10" pipe diameter. The Tritium Extraction System (TER) is placed as close as possible to PbLi BB outlet in order to reduce the tritium inventory into the loop and therefore the tritium leakage into the environment. A tritium extraction efficiency of 80 % would allow the reduction of the tritium concentration in the breeder, nevertheless, due to the huge permeation area of the BB and the pipes, about 40,000m^2, the tritium released into the environment due to permeation must be reduced.

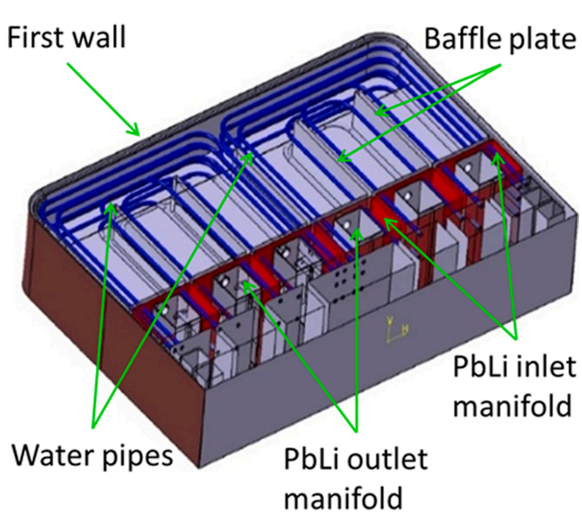

Fig. 1. WCLL BB modules, coating has to be applied externally to the water tubes and on the surface of the First Wall (FW) and baffle plate [1].

The operating conditions and performances required to the coating for the two different applications are summarized in Table 1.

3. Coating technologies

Al-based coatings are presently considered as reference materials for anti-corrosion and anti-permeation barriers on the basis of years of studies about coatings compatibility with PbLi and tritium permeation reduction [6]. As aluminum is activated during the operation of the fusion reactor, with resulting issues at the end of component lifetime, the thickness deposited must be minimised. The target thickness of deposited aluminum is less than 10 μm in order to reduce the amount of activated products to 900 kg for all the BB modules. Alumina can be chemically removed from EUROFER and managed as activated waste: its specific activity reduces to lower than 0.1 GBq/g after about 100 years.

In 2014–2020 three Al-coatings against corrosion, against tritium permeation and as electrical insulation (in PbLi flow) were developed at laboratory scale and a preliminary scaling-up of the technologies was performed. The present fabrication technologies are, PLD (Pulsed Laser Deposition), ECX (chemical deposition) and ALD (Atomic Layer Deposition).

In the PLD technique, a high-power pulsed laser beam is focused inside a vacuum chamber to strike a target of the material to be deposited. Aluminum is vaporized from the target and, as a result, a highly homogeneous layer of alumina is deposited on the EUROFER. The interface is well defined and the external surface is smooth, the manufactured coating shows mechanical properties uncommon for a ceramic, like high plastic deformation in tension [7,8]. This ductile amorphous ceramics (DAC) are which means in between ceramics and glasses, with chemistry similar to the first, structure similar to the second, but with a unique mechanical behaviour: elasto-plasticity at low temperature. Key structural features of DACs are the absence of crystalline order or porosity at any scale and no glass transition temperature (T_g). Al_2O_3--based DAC samples fabricated by PLD, exhibit an elasto-plastic response under both tensile and compressive tests at room temperature. A clear onset of plastic deformation has been observed and a yield stress as high as 4 GPa (tensile and compressive) has been measured, with a plastic deformation as high as 7% in tension and 100 % in compression, Fig. 3.

Starting from 2017/2018, a first optimization step of the deposition parameters was carried out, with the main aim to drastically reduce both the density of defects (growth instabilities and droplets) below 1000 cm^{-2} and their dimension to less than 1 μm, over 30 cm^2. Given that the laser source used has been kept constant (Coherent COMPEX-PRO 205 F, pulse length 20 ns, wavelength λ 248 nm), the parameters which were acted upon were spot size and fluence, together with the mechanics of target motion in order to optimize the ablation process. For a given target, spot size is controlled by the focal distance and its power distribution must be as close as possible to a top-hat shape, in order to avoid low energy regions where incomplete vaporization occurs with the generation of debris and large droplets. Once found the optimal spot size, the laser fluence was optimized in order to maximize deposition rate with minimal droplet ejection. The result of this optimization was the GEN II coating family with a number of defects < 1000 cm^{-2} and a typical dimension of 500 nm. In addition, in 2019, a scale-up of the system was performed (sample size up to 300 mm in length) and a second step optimization process was carried out to further diminish the defect density and size. As a matter of fact, depositing on larger surfaces led inevitably to the production of a larger number of defects, thus another finer optimization process was necessary. Thus, all the deposition recipes were reviewed, and a mask was introduced between the target and the substrate holder in order to filter out the tail of the expanding plume, Fig. 4. In fact, the peripheral parts of the plume are

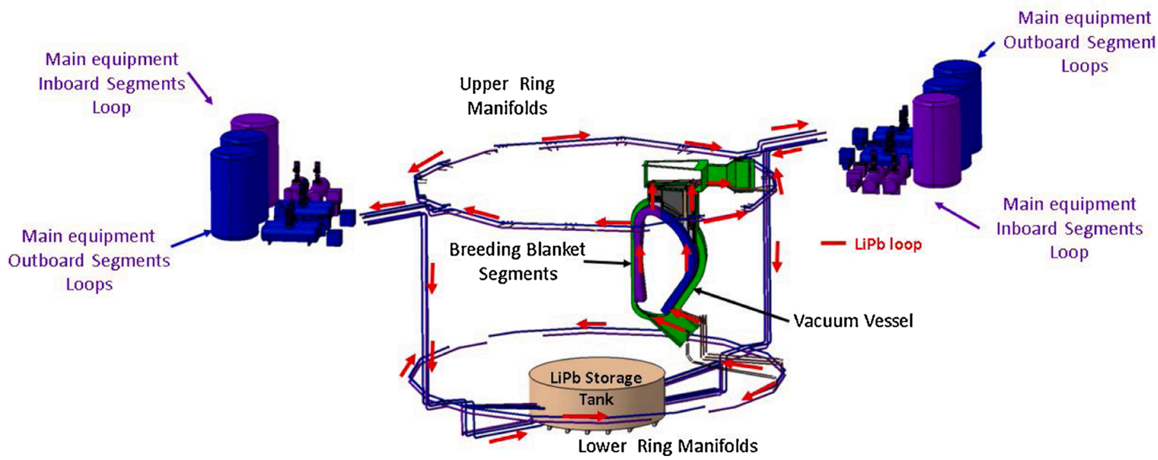

Fig. 2. PbLi loops of WCLL BB.

Table 1
Expected operative condition of coating technologies in the BB and PbLi loops.

Parameter	BB	PbLi loops
Min/Max PbLi temperature at the interface with EUROFER [°C]	290/500	290/330
Tritium and Hydrogen partial Pressure [Pa]	10−500	10−500
PbLi velocity at the interface with EUROFER [m/s]	0.001−0.050	0.05−0.5
Neutron Flux [n/cm^2/s] [1]	1.0 10^{+15}÷1.0 10^{+14}	0
Max Radiation Damage [dpa]	10	<1
Magnetic field [T]	14	0.001
Required Permeation Reduction Factor	>200	10−100

less energetic (causing growth instability) and richer in droplets. This work led to GEN III samples, with less than 10 defects per cm^2 and size below 100 nm and indeed to an optimized coating with zero through defects over an area of 300 × 50 mm^2 for a 3 μm film.

PLD coating can be manufactured at room temperature only on the external surface of the components, therefore, can be applied to the Water Coolant Pipes in the WCLL BB or on a flat surface but cannot be deposited inside the pipes.

The ECX process and the resulting functional surface layers on steel that have been developed and tested in the period from 2014 to 2020 are based upon coating with aluminum and diffusion heat-treatment in argon (Fig. 5) [10]. The latter also produces a thin α–alumina layer on the coating surface. The advantage of this approach is the aluminum reservoir (aluminum in solid solution) underneath the oxide layer, serving as a source of this metal and promoting self-healing in case of local failure of the oxide layer.

Deposition is performed by electroplating, with an ionic liquid serving as the electrolyte. Electroplating is a well-established industrial process for metallic components of various shapes and sizes. The appropriate operating temperature of the ionic liquid is moderate (around 100 °C), the request for dry atmosphere not particularly demanding. The heat treatment is geared to the standard heat treatment of the steel substrate in question, i.e. ferritic/ martensitic material such as Eurofer.

ALD process is a particular Chemical Vapor Deposition (CVD) technique, thanks to which it is possible to obtain continuous and pinhole-free films on substrate with complex geometries (differently from PLD,

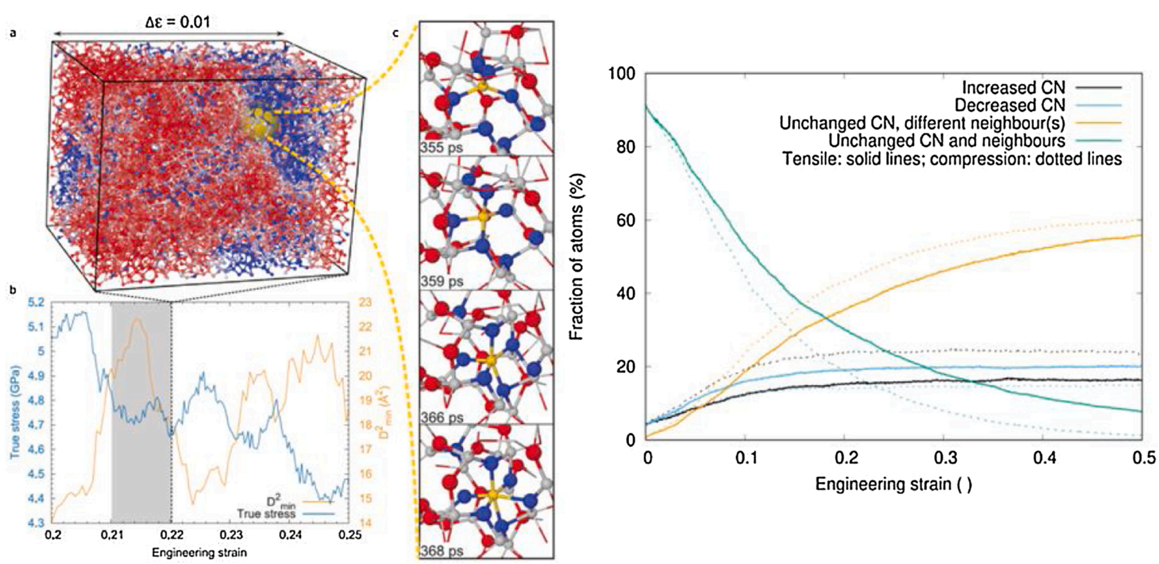

Fig. 3. Atomistic mechanism of room temperature plastic deformation in α-Al_2O_3: (a) Momentary distribution of the local plastic tensile strain at 0.22 strain, where local plastic strain is calculated from the preceding variation in engineering strain indicated by gray color in (b); (c) A single bond-switching event occurring at the edge of a locally yielding atom group; (d) Average changes in bonding during tensile and compressive loading from 0.0 to 0.5 strain at 37.5 × 10^6 s^{-1} strain rate [9]. This figure is licensed under American Association for the Advancement of Science- license Number 5011340539676.

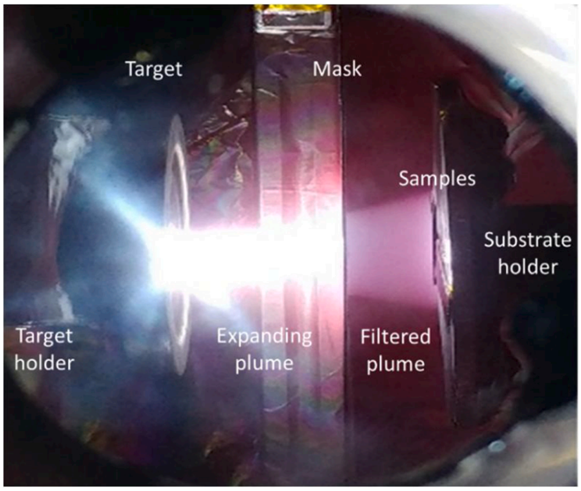

Fig. 4. Picture taken during a deposition run (right) of the effect of the mask in filtering the material in the expanding plume.

which is a line-of-sight technique) [7]. In general, an ALD process consists of a sequence of gaseous pulses of two chemical precursors that react with the substrate in an alternate fashion. The first precursor is pulsed into a vacuum chamber via high speed electro-pneumatic valves, and it is allowed to react with the substrate surface through a self-limiting process that leaves no more than one monolayer at the surface, for a selected amount of time. Subsequently, the chamber is purged with an inert carrier gas (typically N_2 or Ar) to remove any unreacted precursor or reaction by-products. This step is then followed by the second precursor pulse, producing one layer of the desired material, and finally, the system is purged again. This process is then cycled until the appropriate film thickness is achieved, Fig. 6. The cycles for Aluminium Oxide fabrication consist of : a) trimethylaluminum (TMA), i.e. the first precursor, enters the chamber and reacts with the substrate, producing gaseous by products and leaving a functionalized surface; b) Nitrogen is used as carrier gas to purge the system; c) water, i.e. the second precursor, enters the chamber and reacts with the surface of the substrate, producing a thin layer of Aluminium Oxide and gaseous by products; d) Nitrogen is again injected in the reaction chamber to purge the system. These four steps are then repeated cyclically. From this description it is clear that the ALD technique can be effectively used for protective barriers fabrication, but its results are also rather surface sensitive. As a matter of fact, the presence on the substrate of possible organic residues (for example from the cleaning procedure) or native oxides of the steels can hamper the proper growth of the film. It follows that, the substrate preparation will play a crucial role in the development and implementation of this deposition technique.

The main advantage of this technique is the possibility to coat complex geometries at low temperature.

A scale up of ALD system was carried out by ENEA in collaboration with the Italian Institute of Technology (N2E lab., Center for Nanoscience and Technology, Milan) in 2018, the new reaction chamber is 300 mm x 200 mm x 300 mm in dimension, thus small mock-ups of WCS pipes can be coated.

4. R&D activities for coatings characterization

In the period 2014–2020 an optimization of the three technologies for the application to fusion technologies was carried out in order to satisfy the design requirements of good mechanical compatibility with steels, strong adhesion, corrosion compatibility in PbLi at relevant BB design conditions and a Permeation Reduction Factor of at least of 200 under irradiation. A preliminary scaling-up of ECX, PLD and ALD technologies were completed with the final objective to select the reference process (or processes) for the BB and auxiliary system. In 2020–2023 a complete characterization of the first scaled-up technologies will be performed in view of the selection, planned at the end of 2023, and the consequence scaling to the real geometries and components of the selected processes in 2024. To characterize the performances of the coating at relevant scale, a demonstrator mock-up will be coated and characterized in a dedicated facility with flowing PbLi. The proposed programme will continue for the whole DEMO conceptual phase. In the TBM programme several test in TBM geometries are requested if a decision will be taken to introduce these barriers in the WCLL PbLi loop in ITER (Fig. 7).

The following characterization tests were carried out to qualify coating techniques:

a) corrosion compatibility in PbLi in stagnant and flowing conditions;

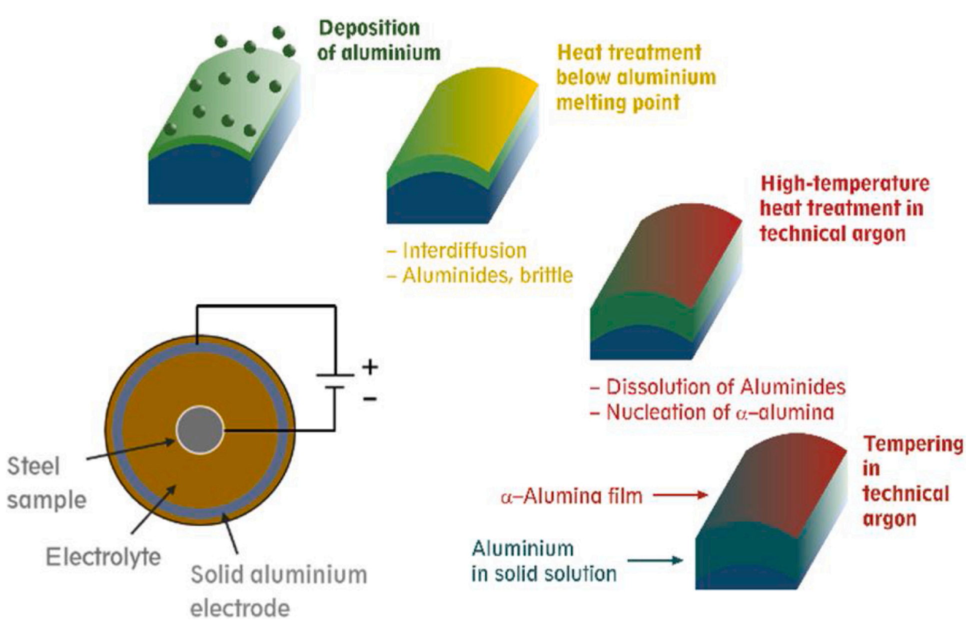

Fig. 5. Illustration of the ECX process consisting of electroplating of aluminum on steel (left) and a three-step heat treatment (right) [10].

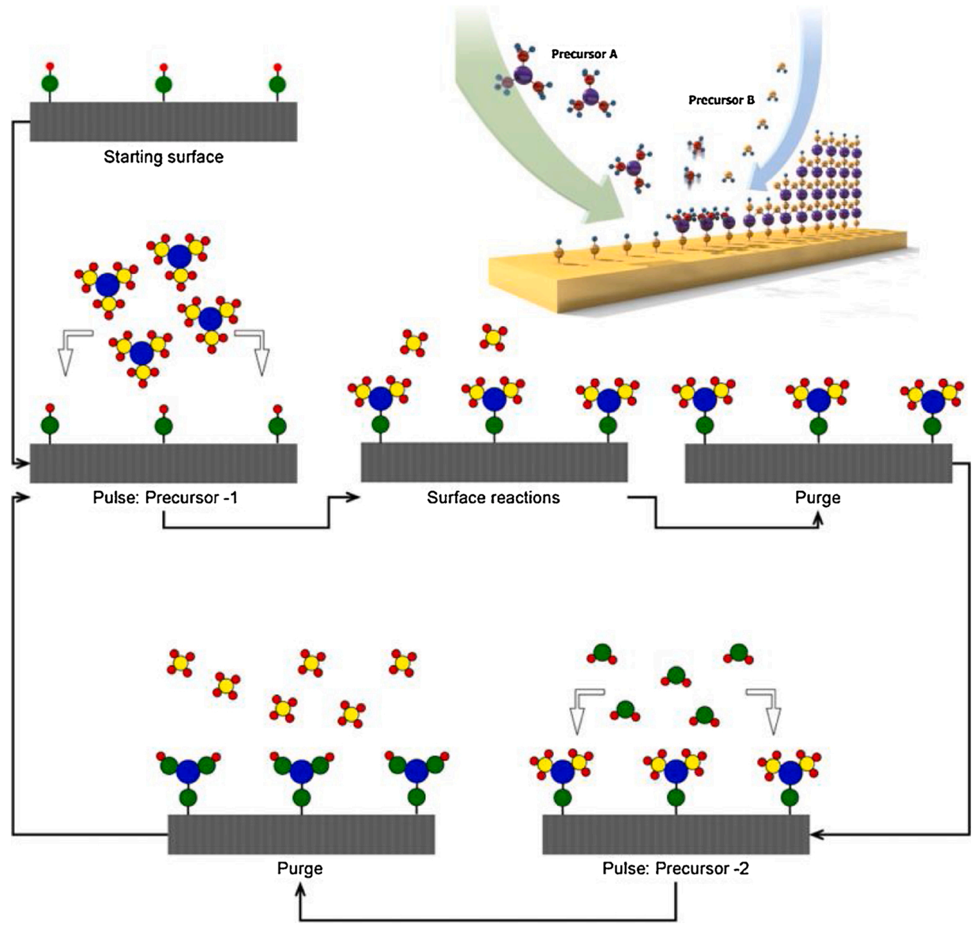

Fig. 6. Schematic representation of the ALD process for Aluminium Oxide fabrication [7].

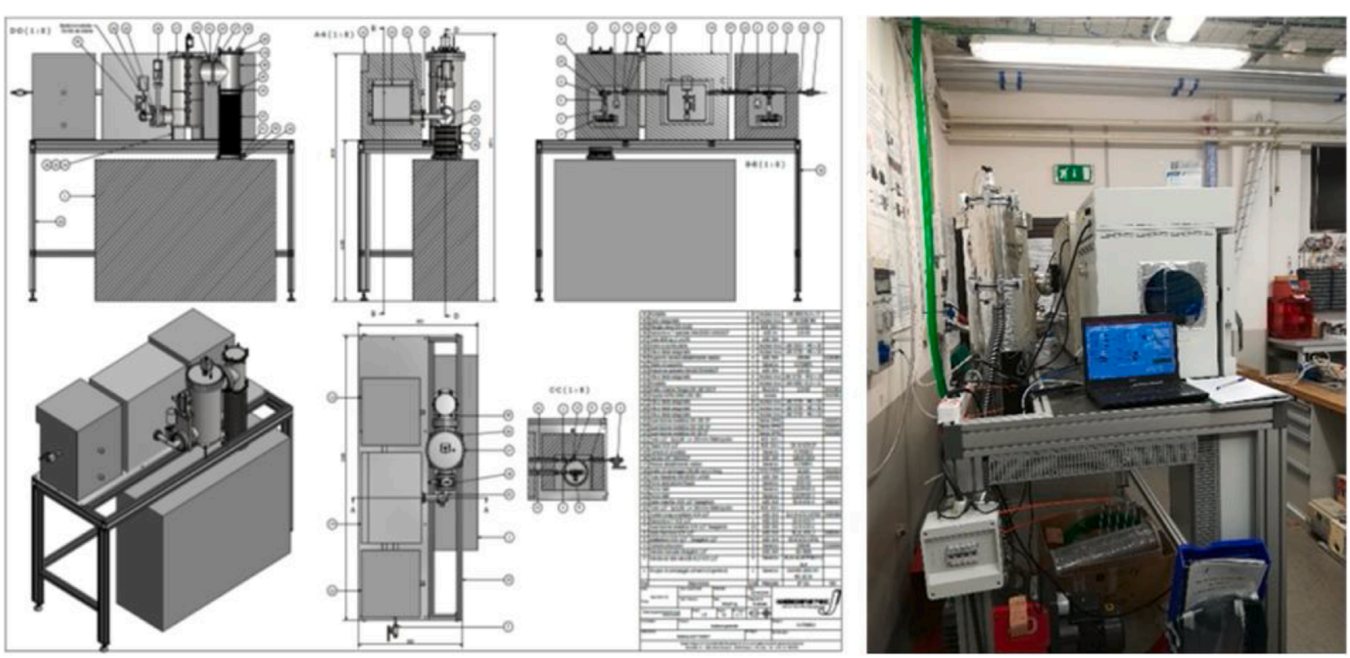

Fig. 7. ALD first scaling-up. The new reaction chamber is 300 mm x 200 mm x 300 mm in dimension, the system was designed in order to be able to host a reaction chamber 1000 mm x 1000 mm x 300 mm.

b) determination of the PRF and evaluation of anti-permeation and anti-corrosion properties in liquid PbLi under electron and γ irradiation;
c) thermal cycle to investigate the structural integrity of the coating in the BB;
d) evaluation of electrical insulator properties of the coating to reduce MagnetoHydroDynamics effect on PbLi flow;
e) permeation tests in PbLi after neutron irradiation in LVR-15 Reactor.

5. Anti-corrosion barriers

In order to determine the compatibility of the coating processes with PbLi, samples have been exposed in stagnant conditions, relevant for BB application where liquid metal velocity is lower than 5 mm/s, and in flowing conditions in PICOLO and IELLLO loops.

ECX coating was characterized in PICCOLO up to 12,000 h at 550 °C and 0.1 m/s, and evaluated in comparison with bare Eurofer. Material loss has been measured as the difference of the diameters before and after contact to the liquid metal. Results reveal a clear decrease in corrosion for ECX-coated Eurofer (Fig. 8), where average 5 μm loss obtained for ECX over the whole time range investigated is indicative for the accuracy of quantification rather than the degradation of the coating [12]. In fact, the accompanying metallographic analysis always shows that the surface layers have remained unaffected which thus is likely to apply also to the thin alumina film at the interface with flowing PbLi, Fig. 9.

In the last years, Aluminium Oxide grown by PLD at the Nano2-Energy Laboratory of Istituto Italiano di Tecnologia (IIT) was deeply tested and characterized. The last generation of PLD coating was also exposed to liquid PbLi in stagnant at 550 °C up to 8000 h in 2018–2019 and in 2020 in flowing conditions at 500 °C up to 2000 h. The temperature discrepancy between the two tests is due to an update of the operative conditions of the WCLL BBs concepts.

The coating managed to protect the substrate from corrosion, also after 8000 h of exposure. The optimization processes lead to the possibility of depositing on large areas, high-quality, defect-free coatings. GEN II coatings did not exhibit exposed steel, thus the coating was able to completely insulate the substrate from the aggressive alloy. The coating itself is intrinsically stable against PbLi at the conditions tested as confirmed by the SEM cross section in Fig. 10. No generalized corrosion occurred during the test, and the nominal thickness of the coating was maintained. It also should be noted that a GEN III batch of samples is nowadays under testing and it is expected to lend even better results.

As a further analysis, X-ray diffractometers (XRD) technique was employed to study the structure of the coating after the test and also to investigate the presence of $LiAlO_2$ on its surface.

Fig. 11 shows the XRD diffractogram obtained from the PLD sample exposed to PbLi (550 °C, 8000 h). The as-deposited PLD grown Aluminum Oxide coatings is known to be amorphous, thus it shows no peaks when studied at the XRD. In addition, this material preserves its amorphous nature up to 650 °C. Considering that the corrosion tests were performed at 550 °C, hence below the crystallization temperature of the coating, it would be expected to still have no peaks in the XRD diffractogram, if not for the ones of the steel substrate and the ones of possible Pb or PbO residues [11]. However, the obtained pattern shows a series of sharp peaks which can be attributed to $LiAlO_2$. In particular, this material is present in more than one phase, thus complicating the recognition of the peaks. Nevertheless, it was possible to identify three main phases of this ternary compound that formed at the surface of the coating: the metastable β-$LiAlO_2$ phase, which is a low temperature stable phase, the $LiAl_5O_8$ stable spinel phase (phase that is poor in lithium) and the metastable α-$LiAlO_2$. It can be guessed that, the $LiAlO_2$ phases forms just at the very surface without affecting the coating in its integrity. In order to validate or refute this hypothesis, Atom Probe Tomography (APT) and X-ray Photoelectron Spectroscopy (XPS) studies are going on. Thanks to these two techniques, it will be possible to understand at which depth lithium was able to diffuse and interact with the material of the coating. The understanding of the changes of the coating occurring during the tests are of paramount importance in assessing the ability of one coating to act as corrosion resistant barrier. For this reason, characterization and thorough analysis of the main properties of $LiAlO_2$ are planned for the next future, especially as it concerns its mechanical properties.

In Fig. 12 shows the results of PLD coating exposed in flowing PbLi for 8000 h: the experimental investigation is ongoing and will be completed in 2021, the first results confirm the adhesion and stability of the coating.

Layers produced by the ALD process are extremely thin and adapt to the surface of the substrate reproducing its characteristics; therefore, the roughness due the finished of the metal or any defect is maintained, Fig. 13. Small defect can be found on coating deposition: an optimization of the substrate cleaning procedure is requested.

The preliminary compatibility test in stagnant PbLi show good compatibility with the eutectic alloy at 550 °C, Fig. 14.

Fig. 15 shows the results of the ALD coating after being subjected to stagnant PbLi for 2,000 h at 550 °C. The photographs clearly show that the substrate is perfectly protected where the coating is applied. Similar effects can be found for the sample subjected to 8,000 h of testing in stagnant PbLi at 550 °C, without observing a greater degradation due to the longer exposure time. An optimization of the cleaning procedure used before starting the deposition is required to eliminate all the

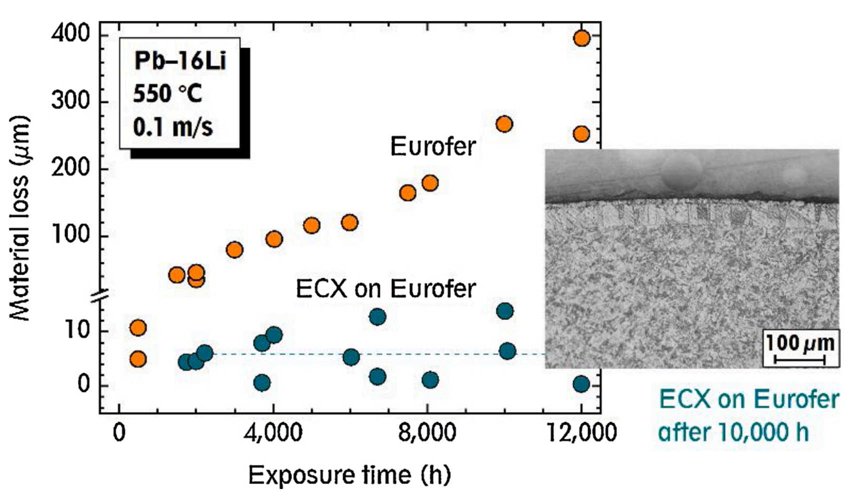

Fig. 8. Material loss measured as the change in sample diameter for Eurofer and ECX-coated Eurofer after exposure to flowing Pb–Li at 550 °C and 0.1 m/s [12].

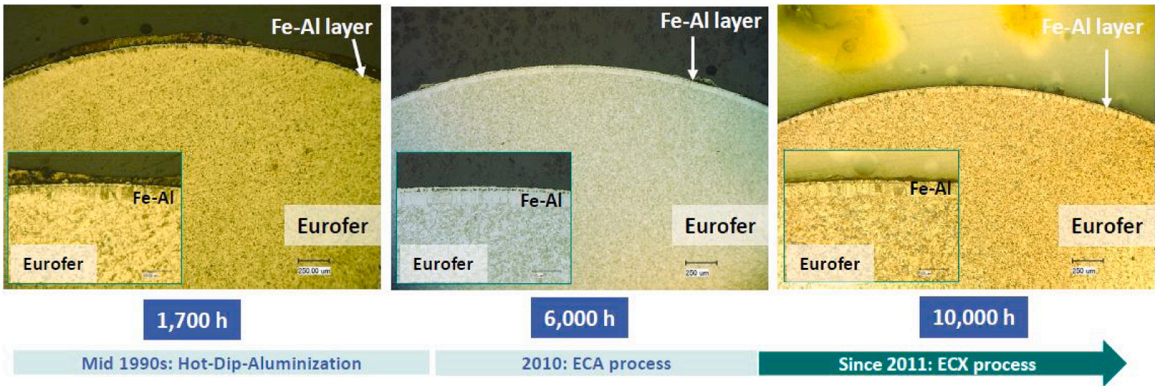

Fig. 9. Scanning Electron Microscopy (SEM) imaging of ECX coating exposed up to 12,000 h at 550 °C and 0.1 m/s [12].

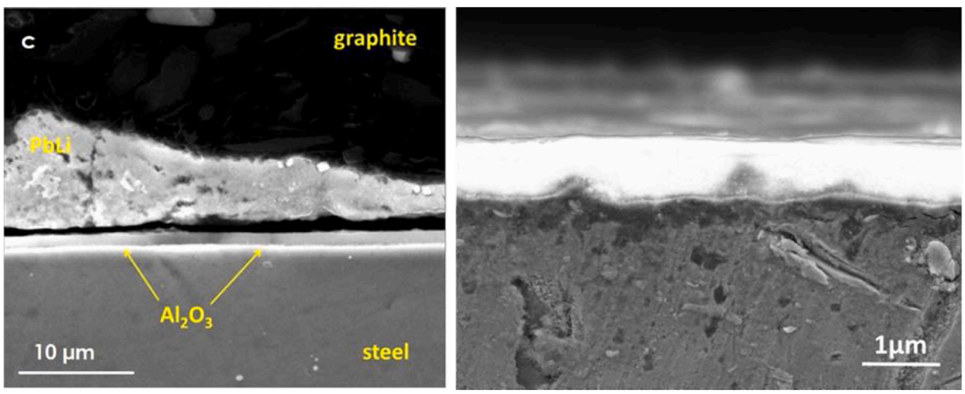

Fig. 10. SEM micrographs cross section of the PLD - Al_2O_3 coating exposed to PbLi (8000 h at 550 °C). The nominal thickness of the resulting film is maintained after the test, demonstrating the ability of the material to resist corrosion [9].

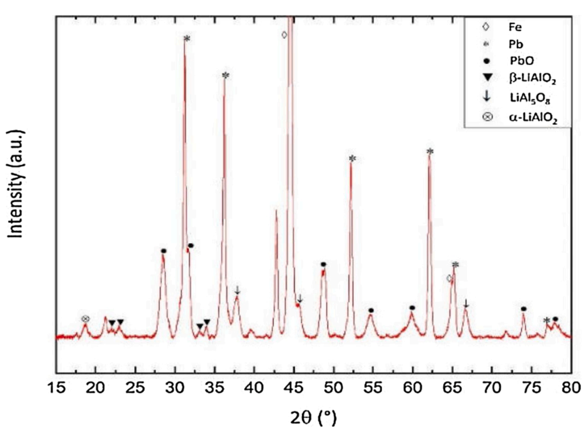

Fig. 11. XRD diffractogram of the GEN II sample exposed to PbLi (550 °C, 8000 h).

possible defects.

6. Permeation characterization of ECX, PLD and ALD coatings under irradiations

Permeation tests were carried out with hydrogen and deuterium instead of tritium in order to determine the Permeation Reduction Factor (PRF) of the coating technologies. Deuterium permeation was also studied before and after being subjected to 1.8 MeV electron irradiation making use of the RIPER facility at CIEMAT for PLD and ECX coating. Instead ALD coating permeation was characterized in 2019 with

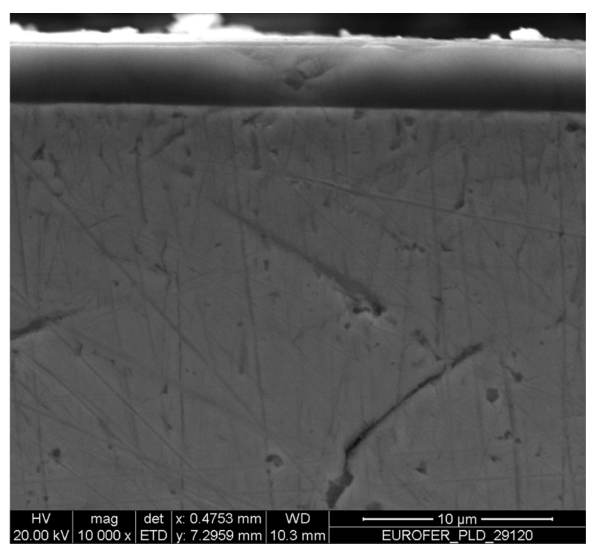

Fig. 12. SEM micrographs cross section of the PLD coating exposed to PbLi at 0.5 m/s, 8000 h at 500 °C.

hydrogen with the support of PERI-II facility at ENEA; the characterization under thermal cycles and electron irradiation is planned for 2021.

The results for deuterium permeation tests (Fig. 16) for ECX coating indicate a permeation reduction in contrast to bare Eurofer by a factor of 50 and 500 at 400 °C and 200 °C, respectively. After electron irradiation, the reduction factor decreases to about 10–100 over the investigated

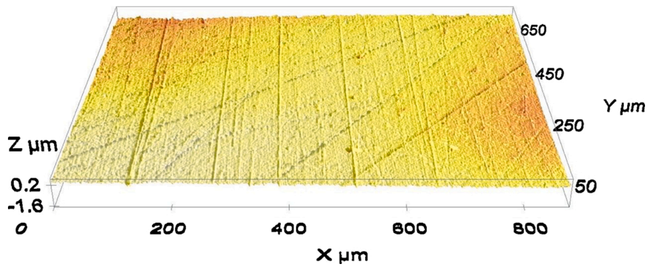

Fig. 13. Surface characteristics of the ALD coating.

temperature range from 60 °C to 400 °C.

The currently limited capability of ECX coatings of reducing the permeation of hydrogen isotopes suggests the necessity of optimizing the process, i.e. the heat treatment and heat treatment atmosphere, for increased thickness of the α-alumina formed on the coating surface, from a few to at least several hundreds of nanometers.

Two thicknesses of PLD amorphous Aluminum Oxide (α-Al_2O_3) coating were investigated, a 5 µm (manufactured in 2018) and a 3 µm (Gen III, manufactured in 2019). The permeation barrier layer was able to reduce the flux of hydrogen isotopes by more than six orders of magnitude (PRF > 10^5 at 450 °C), thus positioning at the state of the art of the design of permeation barriers. In addition, the superior adhesion of the coating on the substrate and its thermal stability allowed the evaluation of the PRF value also under thermal cycles (up to 450 °C with a PRF of about 105), without any sign of degradation of its performances, even after several days of thermal cycling, Fig. 17 [13].

More severe tests were then scheduled, in order to simulate the breeding blanket relevant conditions. Deuterium permeation tests combined with electron irradiation (1.8 MeV) confirmed the PRF previously obtained with H_2 with no irradiation [14]. In addition, the PRF does not decrease under e- irradiation but, actually, it improves, probably due to electrical charges accumulation on the surface of the film that results in a hindered adsorption process. A final set of permeation tests was performed on previously ion irradiated samples.

The samples were irradiated with 22 MeV F^+ (0.01 dpa) and still no variation was found. These series of experiments thus demonstrated not only that the PLD-grown Aluminum Oxide coatings can effectively mitigate the permeation of hydrogen isotopes, satisfying the requirements set by design, but also that their performances are not altered, if not slightly, after both severe thermal cycling and irradiation. Thanks to the drastically improved quality, with negligible defects over large surface areas, an unprecedented PRF higher than 10^5, with negligible temperature dependence, was measured for a 3 µm thick coating, at 450 °C, at the spectrometer instrumental limit.

Permeation test carried out on ALD coating in PERI II facility in the temperature range between 300 °C and 650 °C has shown a PRF higher than 1000. The results has to be confirmed after thermal cycles and irradiation planned in 2021.

Fig. 15. Appearance of the ALD coating after the PbLi test for 2,000 h at 550 °C.

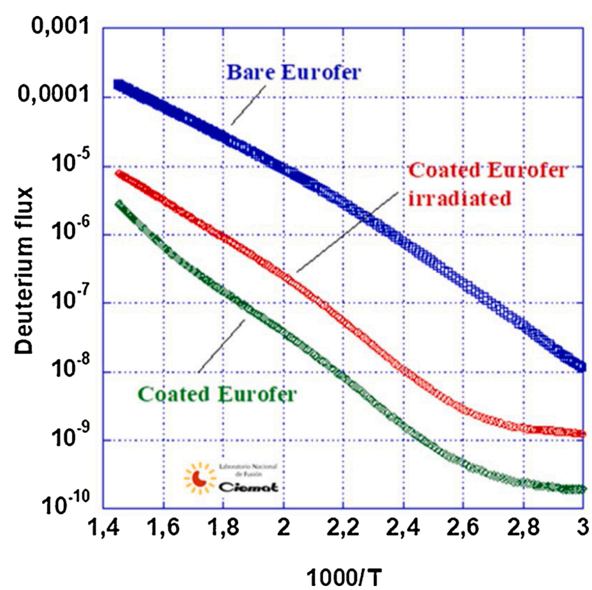

Fig. 16. Deuterium permeation through ECX-coated Eurofer as produced and after electron irradiation in comparison to bare Eurofer.

Fig. 14. SEM micrographs cross section of the Al_2O_3 ALD coating exposed to PbLi (1000 h at 550 °C).

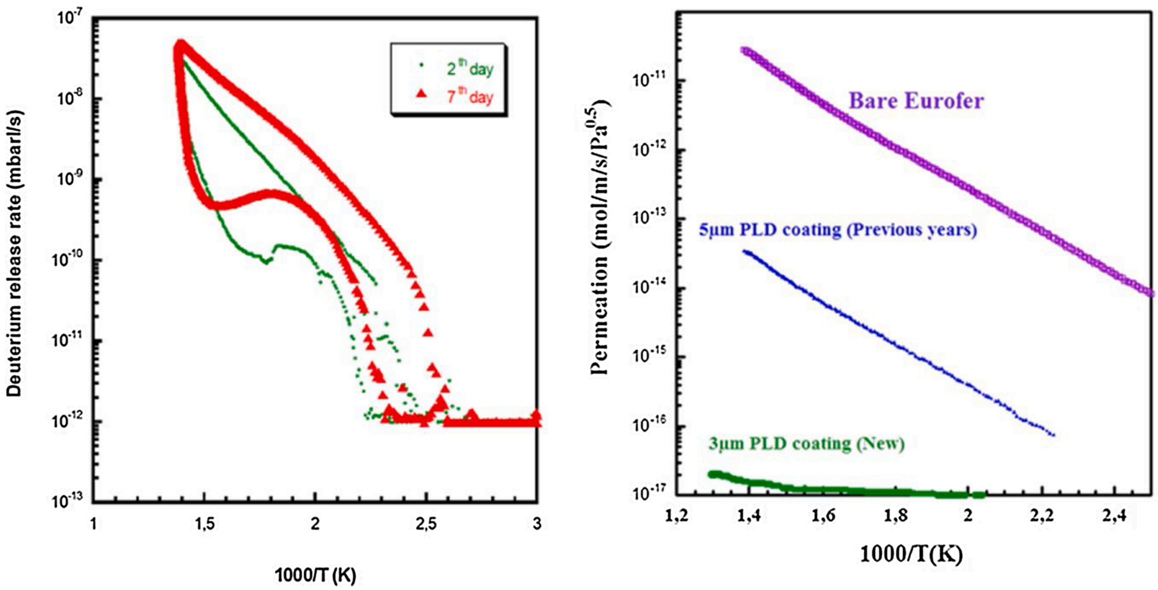

Fig. 17. Results of the permeation tests employing Deuterium: on the left, Deuterium release rate as a function of temperature after 7 days of thermal cycling, showing only a slight modification in the ability of the coating to trap Deuterium; on the right, permeated flux of Deuterium as a function of temperature for a bare sample and the for the samples covered with the two different generations of coatings. An unprecedented PRF value of 10^5 can be observed for the new generation film.

7. Electrical conductivity of the coatings

ECX and PLD coatings electrical conductivity were measured in the temperature range between 20 °C and 750 °C under vacuum and inert gas, Figs. 18 and 19.

The average electrical conductivity of a metal is in the range between 10^6-10^8 S/m, while the one of an electrical insulator is lower than 10^{-8} S/m. In Fig. 18 it is possible to observe that the conductivity value in ECX coating, constituted by an external thin layer of Al_2O_3 and an intermediate layer of Fe-Al, is higher than the value of the alumina (~10^{-13} - 10^{-14}). The conductivity for this coating exhibits low temperature dependency indicating metal like behaviour. In the case of heating in vacuum, the conductivity increases probably due to oxygen reduction.

Currently, ECX coating showed a limited capability of reducing the electron conductivity of the composite, that suggests an application of the coating for the PbLi loops instead of for the reduction of the pressure drops due to MHD effect. The electrical conductivities of PLD-Aluminum

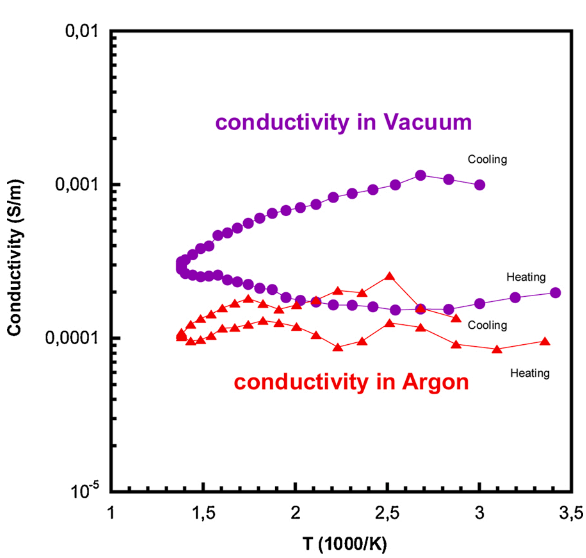

Fig. 18. ECX-coating electrical conductivity.

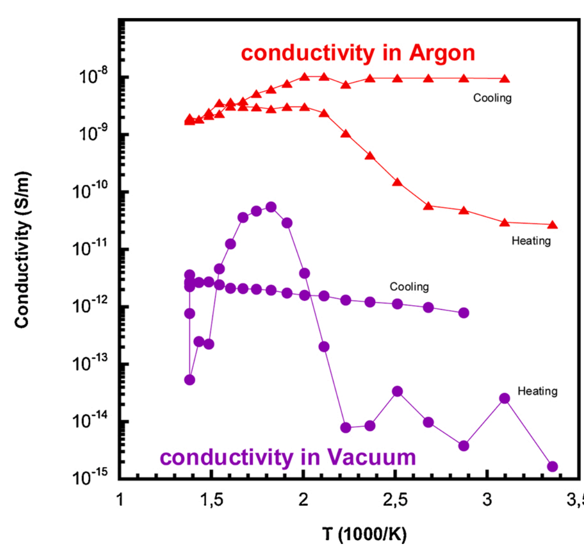

Fig. 19. PLD-coating electrical conductivity in argon and under vacuum.

Oxide coatings, shown in Fig. 19, was evaluated to a value in the order of 10^{-12} S/m at room temperature and in the order of 10^{-11} S/m at 400 °C. The results obtained in vacuum are in accordance with what is expected for alumina. The structure of emission bands is observed in this case, while it is not observed when it is after cooling. Although the coating does not degrade in an argon atmosphere, conductivity is higher than in vacuum. It is reckoned that these values will allow the reduction of the MHD effects to an extent that they will become negligible.

8. Coatings characterization under neutron irradiation

The final test planned in 2020 for the coating characterization under neutron irradiation was carried out in the LVR-15 reactor in CVREZ. The scope of the test was to characterize the PRF of the coating in PbLi under neutron irradiation. For the evaluation of the neutronic conditions, the radiation transport code MCNP6.1 with the nuclear data library ENDF/

B-VII.0 was used. In order to perform the experiment, an irradiation capsule filled with PbLi and mounted with coated and uncoated cylinders, which will be placed in the core of the reactor, was developed in CVR. 2 PLD Alumina-coated sample with 3 μm and 5 μm, 1 ECX Alumina-coated EUROFER samples were exposed to flowing PbLi.

Due to the complexity of the irradiation capsule design and specific operational requirements, the development phase was therefore divided into several steps.

An ex-situ test section was designed and manufactured for verification of the proposed methods of the LiPb capsule cooling. The PbLi flow inside the capsule is generated by natural convection generated by neutron irradiation and tritium production; velocity estimated 1–2.7 mm/s. The gas volumes in the samples and capsule are connected by capillaries to sampling volumes. On the basis of the results obtained, the final test section was manufactured and installed in LVR15 reactor. The experimental characterization test was carried out in 2020. During the tritium permeation experiment with EUROFER coated samples, gas sampling extracted out of the irradiation exposed samples was realized by means of a sampling line. The sampling line was guided towards a specific glove-box located in the reactor hall which is close to the reactor and is connected to the reactor ventilation system.

The tests have shown:

- The PLD-coated samples exhibited a PRF higher than 250 and no corrosion attack from PbLi can be detected on 3 and 5 μm thickness PLD coating. The experiment did not lead to any loss of adhesion or delamination effects at the coating-sample surface, Fig. 20.
- The ECX-coated samples show low PRF compared to not irradiated coatings, maybe due to small cracks developed on the surface. Moreover, some internal pores and voids were found. The base material is intact with no signs of corrosion attack.

9. Investigation methods to check the quality of the coating performed at industrial scale

One critical point in the development of coating process at DEMO scale is the identification of a methodology to check the quality of the coating.

Two methodologies were developed in ENEA/IIT laboratories to qualify the coating at industrial scale. The first, called Thermal Quality Test (TQT), exploits the very high oxidation tendency of EUROFER at temperature higher than 20 °C in presence of oxygen and the barrier properties of the alumina coatings, when flawless. After deposition of the coating, the coated EUROFER is heated up in a muffle furnace at 450 °C for few hours. After cool down, the surface is analysed by optical and electronic microscopy, XRD and RAMAN. Large scale defects are immediately visible, while small scale ones can be spotted by XRD and RAMAN looking for iron oxides. Defects as small as few microns can be found by these techniques. A strict correlation is established between success in the TQT and electrical, permeation and corrosion tests. The TQT test requires an accessible surface, unless X-Ray techniques for complex structures can be used.

The second method developed is called Electrochemical (EQT) that exploits the conductivity of the EUROFER and the high resistivity of the oxide coatings. A part is submerged the in an electrolyte and Electrical Impedance Spectroscopy (EIS) is performed to evaluate the resistance and capacitance of the system. By modelling the data, it is possible to extract an average defect density and coating resistivity on the whole coated component, even of complex shape, such as a BB module.

In order to check the quality of the coating, a detailed methodology and process will be finalized in 2021–2023, when the coating selection will be completed.

10. Conclusion

Within the EUROfusion programme, three aluminum coating techniques were investigated: ECX, PLD and ALD process for the application in DEMO reactor as Anti-permeation, corrosion barrier and to mitigate pressure drops due to MHD effect. In order to demonstrate the capability to scale-up the process from laboratory scale to industrial scale to coat about 40,000 m^2 and 3700 m of PbLi pipes with 10” diameter, a preliminary scaling-up of the processes was carried out in order to coat EUROFER tubes longer than 270 mm. The coatings were characterized from the point of view of chemical compatibility with PbLi, capability to reduce tritium permeation flux and electrical conductivity in order to identify their applicability to DEMO and ITER reactor.

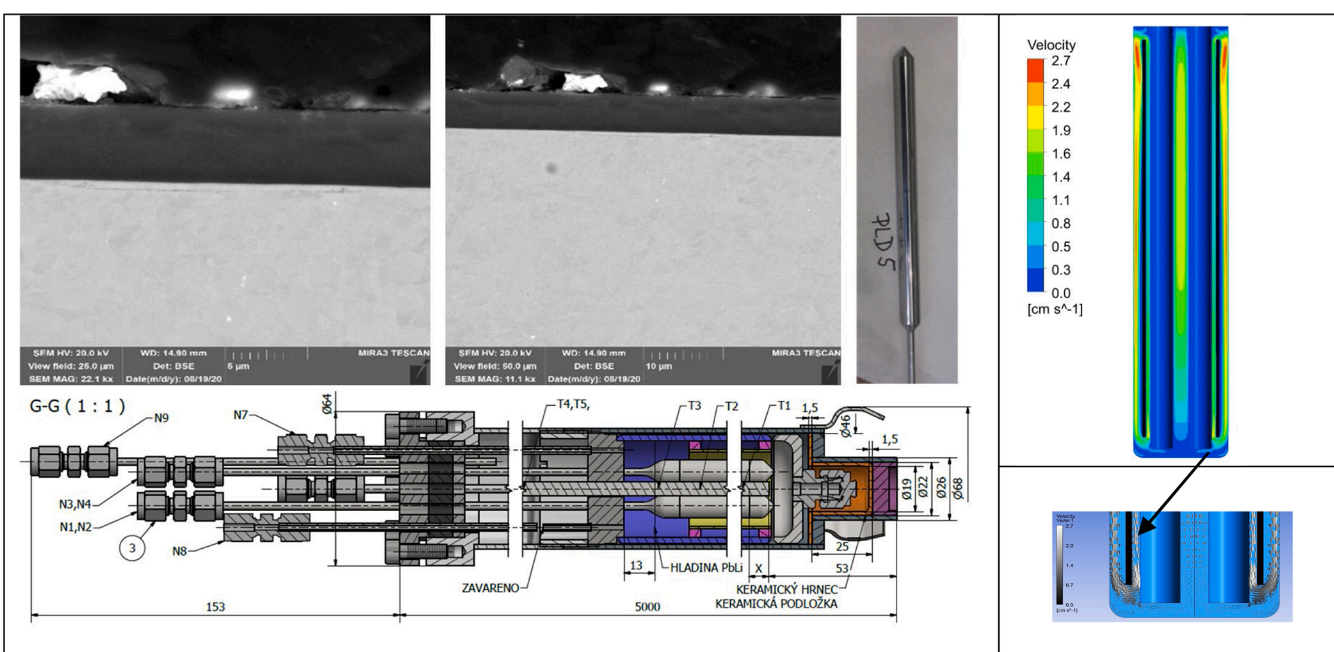

Fig. 20. a) PLD-coating 5 μm exposed in LVR-15 reactor campaign for 620 h at 300÷425 °C in flowing PbLi, b) test section of PbLi irradiated capsule with 4 cylinders, c) Velocity field for non-uniform heating corresponding to the selected position in the reactor (assuming the core located on the left from the capsule) [15].

ECX technique has shown an excellent corrosion stability in PbLi, the experimental results obtained suggests the possibility to use the coating in the PbLi loops pipes.

Corrosion compatibility tests carried out on PLD and ALD techniques have not shown corrosion attack in static PbLi at 550 °C; tests in flowing PbLi is still on-going but the first results have shown good corrosion stability. Moreover, PLD coating has demonstrated to be able to reduce the tritium permeation flux at least of 10,000 under electron irradiation combined with thermal cycles and more than 250 under neutron irradiation. PLD coating, characterized in the temperature range between 20 °C and 450 °C works also as electrical insulator. The main limitation of the PLD process is intrinsic to the technique, it can only coat external surfaces. ALD technology is very promising in terms of capability to reduce tritium permeation flux and the possibility to be applied on complex geometry even at low temperature, however further characterization is required.

The next milestone, to be achieved within 2024, is to identify the best application of the coating technologies developed for DEMO reactor and to perform the scale-up of the processes.

Declaration of Competing Interest

The authors declare no conflict of interest.

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