1. Introduction

Tritium permeation is at the cutting edge of the technological issues related with the development of tritium breeding blanket modules (TBMs) for future fusion systems [1–3]. In particular, it is mandatory to reduce radiological hazards as much as possible, while optimizing tritium balance in the plants. Further issues are brought about if lead-lithium eutectic (LLE) is selected as the breeding material. LLE is extremely corrosive in regard to reduced-activation-ferritic-martensitic (RAFM) steels, which are currently the choice of reference for TBMs. For instance, it is well-established that the corrosion rate for grade EUROFER 97 RAFM steel can be as high as 400 μm yr⁻¹ at 550 °C [4–6]. In order to mitigate tritium permeation and LLE corrosion issues, the fusion...
community relies on coatings as the most promising route available. Ideally, oxide coatings should tackle LLE corrosion and achieve a tritium permeation reduction factor (PRF) as high as 1000 in the gas phase [7–20].

The state of the art in the field of coatings for TBMs is given by Al2O3-forming surface alloys or Al2O3 coatings processed by a variety of techniques. The most studied methods include hot-dip aluminization, chemical vapor deposition, plasma spray, sol-gel deposition, and electrochemical processing [21–26]. Some of the disadvantages of these methods include high processing temperatures, low adhesive strength, low deposition rates, or poor compatibility with complex shapes.

In this work, we utilize pulsed laser deposition (PLD) as the step forward to grow high performance Al2O3 coatings at room temperature. These coatings are particularly interesting due to the unusual combination of metal-like mechanical properties [27], corrosion resistance in high temperature lead environments [28, 29], and excellent behavior under ion irradiation at damage levels as high as 450 displacements per atom [29–31]. The coatings are grown on grade EUROFER 97 RAFM steel, and are tested in regard to thermal cycling and hydrogen permeation in the gas phase as a function of coating morphology (i.e. dense and compact versus columnar or columnar/nanoporous). The most performing morphology is selected to measure deuterium permeation under electron irradiation, and tested in low-oxygen and high-temperature LLE (i.e. 550 °C). The results show that dense and compact Al2O3 coatings grown by PLD achieve a groundbreaking combination of corrosion resistance in high temperature LLE, and hydrogen and deuterium PRFs close to 10^5 at 650 °C (with and without electron irradiation).

2. Methods

2.1. Samples

The substrates used in this work were RAFM steel discs and plates, namely grade EUROFER97. The nominal composition is 8.95Cr–0.18W–0.2V–0.17C–0.048Mn–0.04Si–0.021Ni–0.019Cu–0.0017Nb–0.009Al–0.006Co–0.006Ti–< 0.005P–< 0.001Mo–balance Fe (wt.%). The diameter of the discs is 52 mm, whereas the thickness of the plates is 0.7 mm. The length, the width and the thickness of the plates is, respectively, 40 mm, 8 mm and 3 mm. Prior to the deposition of the Al2O3 coatings, the substrates are ground with SiC paper (P800, P1200, P2400, P4000), polished with diamond paste (1 μm), rinsed and sonicated with deionized water. The coatings are grown on one side on the discs, and on both sides on the plates. The Al2O3 coatings are grown by custom made PLD (manufactured by kenosistec s.r.l) at room temperature in a vacuum chamber (base pressure below 3 × 10^-3 Pa). The pulse energy (410 mJ), the fluence (3.5 J cm^-2), and the repetition rate (20 Hz) are fixed parameters. The laser used is an Coherent® COMPex 205F. More details about PLD system are described in the supporting information, figure S1, of Passoni et al [32]. In order to evaluate the effect of coating morphology on PRFs, three background pressures are utilized during the depositions, namely 0.1 Pa, 1 Pa, and 2 Pa of oxygen (99.9999% purity). The thickness of the coatings is either 1 μm (for corrosion tests) or 5 μm (for hydrogen and deuterium permeation measurements).

2.2. Structural characterizations and thermal cycling

The structural features of the coatings are analyzed in the pristine condition, and after either annealing or thermal cycling by scanning electron microscopy (SEM). SEM observations are done with a field emission (FE) SEM (Zeiss Supra 40) equipped with an Oxford Instruments INCA energy dispersive x-ray spectrometer (EDS), and with a JSM-6010-LV Jeol SEM. The electron voltage is set at 2 kV and 18 kV for imaging, respectively. Thermal cycling is done in a pure Ar atmosphere (99.9999%) between room temperature and 550 °C. The single thermal cycle consists in heating from room temperature up to 550 °C (2 h dwell) at 2 °C min^-1, followed by cooling down to room temperature at 2 °C min^-1. This single cycle is repeated 50 times to simulate DEMO relevant operational conditions.

2.3. Hydrogen permeation measurements

Hydrogen permeation measurements are done using the experimental device ‘PERI II’, described elsewhere [3, 33], evaluated using the continuous flow method (CFM). The device comprises two different sections, separated by a disc sample (either bare or coated) that is kept at a given temperature (i.e. between room temperature and 650 °C) by means of a resistive furnace. During the measurements, one of the two sections is held at low pressures (i.e. section 1, below 10^-5 Pa). The other section (section 2) is held in the same range of pressures until pure hydrogen (99.9999%) is injected, reaching a pressure of 10^4 Pa. At this point, hydrogen permeates through the sample from the high-pressure section, reaching the low-pressure section. A quadrupole mass spectrometer (QMS) in the low-pressure section registers the corresponding ion current, from which the hydrogen flux is derived. The ion current is averaged within cycles of 12 s each. This current (generated by hydrogen ionization on the QMS head), measured at any time, is proportional to the hydrogen permeation flux. Further details on the experimental procedure can be found in [34].

Deuterium permeation measurements are done with the ’radiation-induced permeation and release (RIPER)” facility, coupled with a 2 MeV Van de Graaff electron accelerator, as described in [35]. The measurements are done at 450 °C on pristine samples, and during irradiation with 1.8 MeV electrons. The samples are heated up from room temperature to 450 °C at a rate of 10 °C min^-1. Once, the sample reaches 450 °C, it is electron irradiated for 4.5 h. Then, radiation is stopped and temperature is kept at 450 °C without irradiation. After that, the sample is cooled at a rate of 10 °C min^-1. Although, high energy electrons do not perfectly reflect in core experiments, this procedure is repeated for 7 d. The samples divide the facility in two chambers. On one side is the gas cell where deuterium is introduced (section 1), and on the other side is the coupling to the accelerator (section 2). The two chambers and the sample are sealed together by
copper rings. The samples are heated by a spring-loaded oven inside section 1, and the temperature is measured by a thermocouple welded on the back of the samples in section 2. The measurements begin when deuterium is injected into section 1 through a leak valve. The coated side of the sample faces section 1. The amount of deuterium permeating through the sample is measured by a Pfeiffer smart test (sensitivity around \(10^{-10}\) Pa l s\(^{-1}\)), which is shielded in 10 cm thick lead blocks to prevent radiation damage. The dose rate (held at \(10^2\) Gy s\(^{-1}\)) is proportional to the electron beam current, and is measured by an ionizing chamber mounted in section 2. Section 1 is isolated from the accelerator beam line with a 0.05 mm thick aluminum window. Temperature, pressure, radiation dose rate, and permeation rate are continuously registered.

2.4. Corrosion tests

The corrosion tests are performed in thermal-insulated stainless-steel capsules (AISI 304, \(H = 480\) mm and \(d_{\text{int}} = 134.5\) mm) designed for the exposure of steels to stagnant lead alloys. The aim of the tests is to provide a simple yet straightforward comparison of the performance of uncoated and coated samples. For this reason, neither an active oxygen control nor an accurate assessment of the chemical conditions of the liquid melt are performed systematically. The capsules are heated using band heaters, and contain alumina crucibles \((H = 220\) mm and \(d_{\text{int}} = 125\) mm). These crucibles contain the liquid metal, avoiding contact with the capsule’s steel walls. The capsules have inlets for: (i) a K-type thermocouple (kept inside an alumina tube closed in one end), (ii) a stainless-steel tube used for connecting the capsule with the LLE melting tank, and (ii) 316L specimen-holders. The LLE used for the experiment (approximately 12 kg) has a commercial purity of 99.97% and is supplied by ECOBAT S.p.a.

In order to avoid impurities in the liquid melt as much as possible, Pb–16Li ingots are surface cleaned, and melted in a tank containing a pressurized \((1.8 \times 10^5\) Pa) pure argon (99.9999%) atmosphere at 300 °C. The melt is moved inside the capsules through a tube containing a PORAL filter, and is then heated up to 550 °C in an over-pressure \((1.8 \times 10^5\) Pa) pure argon (99.9999%) atmosphere. This atmosphere has a nominal content of \(10^{-3}\) wppm H\(_2\)O and \(5 \cdot 10^{-4}\) wppm oxygen. Therefore, the tests are carried out far from oxygen saturation, and might even take place under dissolutive conditions with respect to the stability line of alumina in Ellingham’s diagram. Finally, the samples are inserted in the liquid melt. Extraction is done after 1000 h. The samples are left to cool inside the capsules at 2 °C min\(^{-1}\). The tests are done in static LLE conditions.

3. Results and discussion

3.1. Hydrogen isotopes permeation results

The aim of the experiment is to verify with the available means that the PLD-grown alumina coating is able to provide protection of eurofer 97 steel in DEMO relevant conditions. Different morphologies are considered by tuning the deposition background pressure from 0.1 Pa up to 2 Pa keeping 5 μm as selected thickness. The SEM images in figure 1 show the different morphologies of the as-deposited Al\(_2\)O\(_3\) onto eurofer 97 steel at different O\(_2\) background pressure. As described in literature, the 0.1 Pa, figures 1(a) and (b), deposited sample are clearly fully dense, homogeneous, smooth and without open porosity. At higher background pressures, figures 1(c) and (d), film density decreases monotonically with the appearance of columnar features first and open vertical porosity then, figures 1(e) and (f) [36].
Hydrogen permeation rates are measured in CFM mode by means of a QMS for different kinds of coatings morphologies at different temperature (350 °C, 450 °C and 550 °C).

In this study, the figure of merit for the PLD-grown alumina coatings is the permeation reduction factor (PRF), defined by the ratio of hydrogen permeation flux through the uncoated sample and hydrogen permeation flux through the coated samples. Figure 2 shows a typical QMS spectrum recorded at 550 °C and 10^4 Pa of hydrogen partial pressure in terms of ion current (A). Examining the permeation rate evolution from starting at 0 cycles up to the end of the measure, it is clear how the behavior of materials (both bare and coated) is almost the same. In fact, after the background measure (at least 500 cycles) hydrogen is loaded at 10^4 Pa and a new steady state flux is reached in a short time and does not change during the measure. Furthermore, for all samples the steady state fluxes after the hydrogen injection have in common an average higher value that underline a permeation process through the materials. Overall, measurements show a continuous decrease of the measured permeation rate with decreasing deposition pressure (i.e. obtaining the best performance for the fully-dense and compact alumina coating) as shown in figure 3(a). In fact, columnar morphologies, obtained at higher background pressure, define preferential pathways (i.e. open porosities) for hydrogen atoms that may diffuse more easily through the barrier coating resulting in higher permeated flux values.

At the same time, figure 3(b) shown an exponential increase of the PRF with the temperature. Looking more in detail, it is worth highlighting that the permeation of hydrogen through the bare steel sample is negligible at low temperatures below 350 °C. For increasing temperatures, the hydrogen flux through bare steel dramatically increases, while it is almost constant for the coated samples; hence, the PRF increases up to 10^3, well above the DEMO requirement of 10^3.

These results underline the effectiveness barrier behavior of PLD-grown alumina. Furthermore, the effectiveness of the barrier also depends on the integrity of the coating. Cracks and defects can decrease the quality of the protection layer and the hydrogen atoms can permeate easily through the base material [22, 23, 37–40]. According to these results, we focused on 5 μm thick Al2O3 coatings deposited at 0.1 Pa, further optimizing the process to minimize the number and the size of the droplets and defects present in the coating [41, 42].

Also, to evaluate coating behavior upon thermal cycling, the optimized coated samples were subjected to 50 cycles from 250 °C to 550 °C in Ar, as to simulate the pulsed behavior of a hypothetical DEMO reactor work cycle. The permeation barrier characteristics of the coatings are substantially maintained, as shown in figure 4, even if a slight increase of permeability is observed after the thermal cycles.

Nevertheless, the coated samples exhibit a remarkable PRF value of above 10^4. SEM analysis performed on pristine (figure 5(a)) and thermally cycled (figure 5(b)) reveal no cracks or delamination over the all coated surface.

A more detailed analysis, ascribe the deterioration of the performance in the thermally cycled samples to the formation of submicron sized pinholes formed upon detachment of process-related defects, called droplets, upon the thermal
challenge [43]. Even if we estimate that only a small fraction (in the range 0.1%–1%) of the surface is affected by these pinholes, they might be the cause of the decrease in PRF observed due the mechanism described by Sawada et al [44]. Further, the optimized Al_2O_3 coatings were tested for D_2 permeation upon electron irradiation at 450 °C, in the RIPER facility, confirming that reduction in permeation with respect bare steel is comparable to the unirradiated case with H_2, as shown in figures 6(a) and (b). In fact, for the uncoated sample a deuterium permeation rate close to 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} is found, while a lower value of about 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} is measured for the coated ones, both considered at 450 °C. Finally, in order to evaluate the robustness of the coating, deuterium permeation tests were continued for 7 d for 7 thermal
and irradiation cycles, figure 6(c). It is observed that the formation of desorption bands during the heating ramp is due to the release of trapped deuterium. Also, a slight increase of deuterium permeation rate at 450 °C is observed (going from $3 \times 10^{-8}$ mol m$^{-2}$ s$^{-1}$ to $5 \times 10^{-8}$ mol m$^{-2}$ s$^{-1}$) but keeping a PRF value close to $10^3$.

3.2. Corrosion in static Pb–16Li

As a first corrosion test in static lead lithium eutectic Pb–16Li, LLE, we chose to expose uncoated and coated (1 μm thickness) eurofer 97 steel samples at 550 °C in pure argon atmosphere for 1000h. The uncoated sample is visibly corroded (figure 7(a)), while the coated sample is protected (figure 7(b)). Microscopically, the typical dissolution-corrosion attack of eurofer 97 by LLE through grain boundary attacks is evident [45], while the coated surface is completely protected from corrosion as shown in figure 7(b). In particular, the cross-sectional SEM analysis (figure 7(b)) reveals the presence of the coating without cracks, delamination phenomena or thickness reduction. It is worth noting that in these experimental conditions Al$_2$O$_3$ would be expected to interact with the Li present in the LLE, being reduced, hence, even if these preliminary results suggest that alumina coatings perform also as corrosion barrier in LLE, longer corrosion tests are needed to verify its actual stability in LLE.

4. Conclusion

In this work, bare and alumina PLD-coated eurofer 97 steel disks and plates are evaluated as protective barrier to DEMO relevant conditions. In particular, coated disks are tested by means PERI II facility in order to qualify alumina as anti-permeation barrier. By optimizing the deposition process for the fully dense and compact film an unprecedented PRF well above the DEMO requirements. All permeation results are also in good agreement with the work carried out with RIPER facility under 1.8 MeV electron irradiation. Moreover, PLD-grown alumina coatings retain structural integrity, adhesion and barrier properties upon long thermal cycles and irradiation. Finally, a preliminary short term (1000h) corrosion test in LLE at 550 °C underline a good protection of the steel against dissolution-corrosion. However, the experiment conditions do not perfectly reflect DEMO environment, the combination all of these features with interesting mechanical results obtained in a separate study [27] makes alumina thin film produced by PLD an interesting coating to protect structural materials in harsh conditions.

Acknowledgments

The authors acknowledge partial financial aid by the Italian framework program AdP MiSE-ENEA project B3.1-PAR 2015 and by the EU project TRANSversal Actions for Tritium, TRANSAT, GA # 754586.

Addition information

This work contributes to Sub-Program 3 (SP3) of the Joint Program on Nuclear Materials (JPNM) of the European Energy Research Alliance (EERA).

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