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Long-term corrosion behavior of Al-based coatings in flowing Pb–15.7Li, produced by electrochemical ECX process

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ABSTRACT

RAFM-steels such as Eurofer are considered as structural materials for breeding blankets in future fusion power plants (DEMO). Some of these blankets e.g. HCLL, WCLL and DCLL, use flowing Pb–15.7Li as liquid breeding material. In these concepts, the breeding material will be in direct contact to the structural material at operational temperatures of up to 550 °C. However, bare RAFM steels suffer from strong corrosion attack with corrosion rates between 100 and 400 µm under these conditions. To protect bare RAFM steels from corrosion, Al-based coatings are considered as corrosion barriers. Different coating processes were developed in the past, with focus on electrochemical processes within the last decade. The currently most promising one is the so-called ECX process. Based on the electrodeposition of aluminum from an ionic liquid, it produces smooth and uniform Al enriched scales. These ECX coatings have already shown good short- to mid-term corrosion resistance in flowing Pb–15.7Li for up to 4000 h.

In the current study, the long-term corrosion behavior of aluminum-based coatings on Eurofer made by ECX process was investigated. Exposure times of up to 10,000 h in flowing Pb–15.7Li were reached under fusion relevant conditions, i.e. 550 °C and a flow velocity of 0.1 m/s. In comparison to bare Eurofer the corrosion attack is drastically reduced while corrosion rates lay below 20 µm/a. Additionally, it was found that the corrosion behavior is also superior to the corrosion behavior of Al-based barriers produced by the ECA process after long-term exposure in Pb–15.7Li.

1. Introduction

The application of functional coatings, e.g. aluminum-based coatings, is considered to show a beneficial impact on the performance of different blanket concepts [1,2]. On one hand these coatings should reduce the tritium permeation through the structural material, i.e. low activation ferritic martensitic steels (RAFM steels), and on the other hand, they should reduce the occurring safety concerns resulting from the poor corrosion behavior of RAFM steels significantly. Especially in the case of blanket designs such as HCLL, DCLL and WCLL, that use the liquid metal alloy lead-lithium (Pb–15.7Li) as breeding material, RAFM steels are supposed to be in direct contact with flowing Pb–15.7Li at demanding operation temperatures of up to 550 °C [3,4]. Under these conditions several corrosion studies revealed high corrosion rates for a variety of RAFM steels e.g. Eurofer, MANET, F82H-mod., and CLAM in the past [5–7]. In flowing Pb–15.7Li high corrosion rates between 80 µm per year and 400 µm per year were reported depending on flow velocity and testing temperature [5,8,9]. Besides safety concerns coming from the degradation of the structural material, risks and operation instabilities may arise due to the occurrence of high amounts of corrosion products that in turn could lead to the formation of precipitates. As a consequence, tubes and channels could be plugged inside a blanket system [10].

To reduce these corrosion related effects, aluminum-based coatings were identified to be able to protect RAFM steels from corrosion in Pb–15.7Li [11,12]. In 2002, Glasbrenner et al. already showed the potential of aluminum-based coatings produced by hot dip aluminization (HDA) with a subsequent heat treatment, to protect coated RAFM steels such as MANET and Eurofer from corrosion in flowing Pb–15.7Li [13]. However, the HDA process showed some disadvantages e.g. a relatively high thickness of the coatings (low activation criterion).

To fabricate thinner and more homogeneous aluminum-based coatings, two electrochemical processes have been developed during the last years [14]. The so called ECA is based on the electrodeposition of aluminum from volatile, flammable organic solvents. Long-term corrosion tests in flowing Pb–15.7Li revealed that these thinner coatings are able to protect Eurofer from corrosion for up to 12,000 h at 550 °C and a flow velocity of 0.1 m/s [15]. However, despite of the

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Fig. 1. Fabricated corrosion test samples of Eurofer after different fabrication steps: As coated (1), after 1st HT step (2) and after the 3rd HT step (3).

sufficient ability to protect the underlying steel, coatings made by the ECA process showed some inhomogeneous corrosion attack of the coating itself [15]. Besides this, the variation of process parameters of the ECA process is limited and safety restrictions are challenging due to the high reactivity of the chemicals and aluminum compounds used in this process [16].

Therefore, a second electrochemical process, i.e. the ECX process, was developed. This process is based on the electrodeposition of aluminum from ionic liquids. Through the improved controllability of this process, aluminum deposition rates of up to 25 µm/h could be reached. Additionally, the uniformity and the achieved morphology of the deposited aluminum layer could be improved by applying pulse plating techniques [16,17]. Coatings made by ECX process showed smooth and fine grained surface structures that showed an improved behavior during the mandatory heat treatment procedure compared to Al coatings made by the ECA process [16]. During short-term corrosion tests in flowing Pb–15.7Li aluminum-based coatings on Eurofer steel obtained by ECX process have already proven their ability to reduce corrosion rates drastically compared to bare Eurofer steel under fusion relevant conditions, i.e. test temperature of 550 °C and a flow velocity of 0.1 m/s. Additionally, these coatings exhibited an improved corrosion behavior in comparison to ECA coated Eurofer for exposure times of up to 4000 h [18].

In addition to this previous study, the current study presents results for the long-term behavior in flowing Pb–15.7Li of thin aluminum-based coatings on Eurofer fabricated by the electrochemical ECX process with achieved exposure times of up to 10,000 h.

2. Experimental

2.1. Fabrication of Fe–Al coatings by the ECX process

The fabrication of aluminum-based coatings made by the ECX process consists of two basic process steps: First, a pure aluminum layer is electrodeposited from an ionic liquid (IL) on a RAFM steel substrate. And second, a subsequent heat treatment (HT) including three different stages is performed to form the desired protective Fe–Al scales.

2.1.1. Electrodeposition of aluminum from an ionic liquid

In this study pure aluminum layers were electrodeposited from commercially available ionic liquid consisting of a mixture of 1-ethyl-3-methyl-imidazolium chloride ([Emim]Cl) and $AlCl_3$ (ratio 1:1.5). The IL was delivered by *BASF SE*. The electrolyte was used without further purification. As substrate standardized rod shaped Eurofer corrosion test samples with a diameter of 8 mm were used. The geometry was the same as in previous corrosion test campaigns performed in PICOLO loop [5,15,18].

The samples were carefully grinded with SiC (1000 grade) abrasive paper. Afterwards they were electrochemically degreased and cleaned in a sodium hydroxide-based electrolyte. Following this pretreatment, the samples were transferred into a glove box which contained the set-up for electrodeposition of aluminum. The electrodeposition was performed in a glass beaker of approx. 300 ml volume. During the electrodeposition, the prepared Eurofer test samples acted as cathode and a ring-shaped pure aluminum sheet (*Puratronic 99.998%*, Fa. Alfa Aesar) as a dissolving anode. For controlling the electrochemical process, a pure Al-wire was used as a quasi-reference electrode.

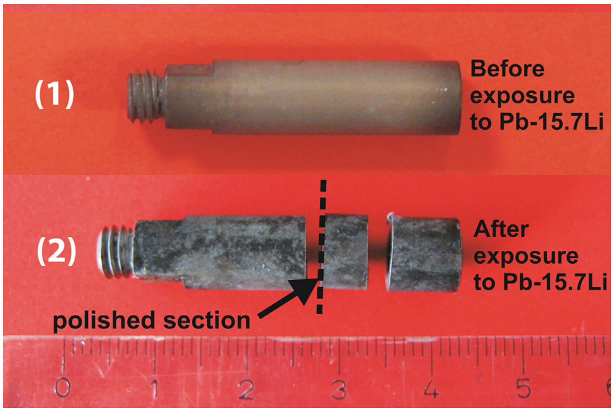

Fig. 2. Appearance of a ECX coated corrosion test sample prior (1) and a long-term exposed sample after cutting (2) prior to the metallographic preparation.

Prior to the Al deposition itself, the open circuit potential (OCP) was measured and the sample was polarized anodically ($j_a = 10\,mA/cm^2$) for 45 s in order to improve the reliability of the activation of the steel substrate, and thus the coverage and adhesion of the applied aluminum coating [19].

Similar to a previous study, pulse plating was used for aluminum electrodeposition, with a current density of 40 mA/cm^2 during the pulse and 0 mA/cm^2 during the off-phase of the pulse [18]. The on and off duration was 0.5 s, respectively, and the theoretical mean current density was 20 mA/cm^2 accordingly. The complete deposition time was 30 min.

2.1.2. Heat treatment and characterization prior to the corrosion experiment

The mandatory heat treatment was performed under argon atmosphere in a tube furnace by applying the three-step HT procedure developed by Konys et al. [20]. In this procedure the first step is performed at 640 °C for 4 h, followed by a step at 980 °C for 0.5 h and finally a holding step at 760 °C for 1.5 h. This HT procedure was very similar to the HT performed during fabrication of the ECX coatings used for short-term corrosion tests in flowing Pb–15.7Li as reported in [18]. Fig. 1 depicts the appearance of coated Eurofer test samples after the different fabrication steps.

After the final heat treatment step, diameters of the test samples were measured with a laser scanning device described in more detail in [18]. The obtained diameters D_i served as initial values for evaluating the corrosion rates and the material losses of exposed ECX coated samples after long-term exposure in flowing Pb–15.7Li in PICOLO loop.

2.2. Corrosion testing in flowing Pb–15.7Li

Identical to the previously published short-term corrosion testing campaign on ECX coatings and bare RAFM steels, the long-term testing was conducted in the PICOLO-loop as well, that is operated at KIT. PICOLO loop is a non-isothermal forced convection loop with a maximum temperature of 550 °C within the test section and a minimum temperature of around 350 °C in the cold leg of the loop. Main components e.g. electromagnetic pump, flow meter and the magnetic trap are part of the cold leg. Within the test section, the Reynolds number is approx. 7700 and therefore the flow is in a transition regime with tendency to turbulent flow. The flow velocity in the test section is 0.1 m/s and the overall flow rate in side of the loop is 55 l/h. Additional characteristics of PICOLO loop are published elsewhere e.g. constructional issues in [5,21,22] and temperature, flow conditions in [23–25].

The completion of this first long lasting campaign on ECX coated Eurofer with exposure times of up to 10,000 h allows to directly compare the long-term corrosion behavior of these ECX coatings with bare RAFM steels [5] such as Eurofer and CLAM and additionally with ECA coated Eurofer as well [15]. For all materials mentioned, the experimental set up was kept constant i.e. a temperature of 550 °C in the test section of PICOLO and a flow velocity of Pb–15.7Li of 0.1 m/s inside the gap between the inner wall of the test section and the rod-shaped samples. As in previous test campaigns, twelve samples were screwed together to one stack, which was immersed into the test section of PICOLO loop. The test section itself was located in a glove box system containing argon as protecting gas to avoid / reduce oxygen access to the liquid metal. After rather long exposure times of approx. 6000 h, 6800 h, 8000 h and 10,000 h, ECX coated Eurofer samples were removed from the loop for analyzing their corrosion behavior.

2.3. Characterization after exposure to Pb–15.7Li

Disks of approx. 5 mm thickness were cut from the middle part of the exposed samples, as depicted in Fig. 2. Afterwards, metallographic cross-sections of these discs were prepared by standard metallographic techniques like grinding and polishing.

After polishing a thin layer of gold was sputtered onto the cross-section to allow SEM/EDS analysis. EDS line scans were performed for each sample at four different positions (every 90°) to evaluate the chemical composition of the Fe–Al coating after exposure.

After the SEM investigations, the gold layer was removed by polishing and the cross sections were chemically etched to develop the microstructure. The etching was performed in a modified solution of Vilella´s reagent consisting of ethanol, sulfuric acid and picronitric acid for approx. 20 s. Subsequently the etched metallographic cross sections were evaluated by optical microscopy and SEM/EDS.

The post exposure diameter D_a was determined for each prepared cross-section by moving the sample under the microscope laterally from one side to the other with the help of a micrometer screw (accuracy of approx. < 1–2 µm). After each measurement, the sample was turned by 15° and the diameter measurement was repeated. This procedure was iterated 12 times until a rotation by 180° was reached and 12 diameter values were obtained for each sample, see [18]. The difference between the initial diameter $\mathrm{D_i}$ and the mean diameter $\mathrm{D_a}$ from all 12 measurements represented the total material loss. In addition, the radial material loss (in µm) was determined and a radial corrosion rate C (in µm/a) was derived with the equation given in [18].

3. Results and discussion

3.1. Long-term corrosion behavior of ECX coated Eurofer samples

The examined cross-sections of long-term exposed ECX coated Eurofer samples showed very good corrosion resistance against flowing lead-lithium in all cases even after exposure times of up to 10,000 h. For all examined cross-sections the aluminum-based scales made by ECX process withstood the corrosive environment and protected the underlying Eurofer steel from corrosion. As depicted in Fig. 3, the coatings remained homogeneous and smooth around the rod-shaped Eurofer substrates without local failures such as delamination, or obvious cracks after exposure times of 6000 h and 10,000 h respectively. The overall thickness of the Fe–Al coatings was determined to be above 50 µm in all cross-sections.

The surfaces of the long-term exposed coatings as shown in Fig. 4, were not roughened, which is similar to ECX coatings after short exposure times [18]. Even in comparison to cross-sections in the state as-fabricated, as shown in [18], the surface appeared almost unaffected after exposure times of up to 10,000 h. These findings differed clearly from the appearances of cross-sections of aluminum-based coatings fabricated by other processes like HDA and ECA. After long-term exposure to flowing Pb–15.7Li, these coatings showed partly inhomogeneous corrosion attack [15, 22].

The evaluation of the material loss by measuring the “shrinkage” of the samples diameter as described in section 2.3, revealed radial material losses between 1 and 14 µm for the long-term exposed samples as depicted in Fig. 5. The picture also includes the determined radial material losses after short-term exposure (< 4000 h) as given in [18]. More or less all measured radial material losses lay within a scattering band of around 6 µm ± 4 µm indicating on average a rather stable corrosion behavior even during long-term exposure to flowing Pb–15.7Li. The distribution of material loss values beyond the observed scattering band can be traced back to slightly different surface conditions prior to exposure caused by the batchwise execution of the heat treatment, i.e. the examined samples have not been processed together in a single heat treatment procedure.

The corresponding radial corrosion rates for the long-term exposed samples > 6000 h, also depicted in Fig. 5, varied between 1 µm/a and 17 µm/a. Even when taking the scattering of the radial material loss values and the deviations in the calculated corrosion rates into account, a slight decrease was observed depending on the exposure time. The corresponding determined corrosion rates ranged between 5 and 12 µm/a after an exposure time of approx. 10,000 h, which is roughly

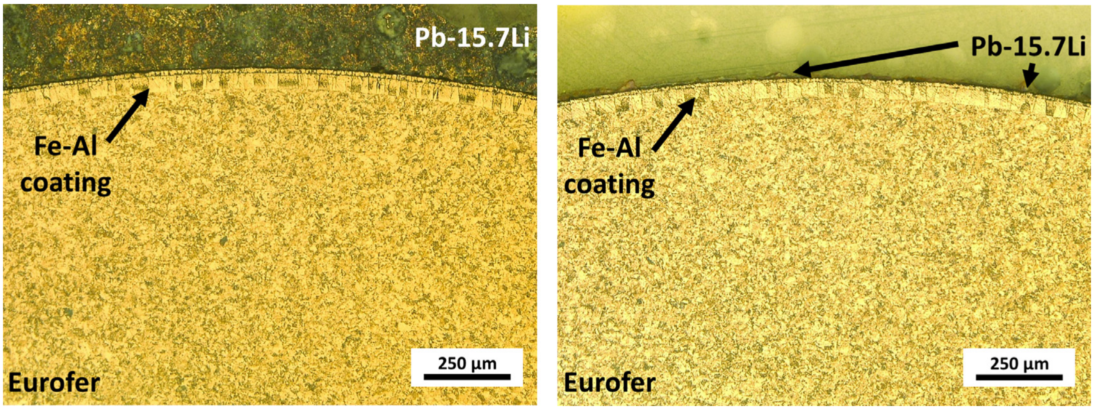

Fig. 3. Cross-sections of ECX coated Eurofer samples after different exposure times in flowing Pb–15.7Li (0.1 m/s, 550 °C): 6026 h (left) and 10,022 h (right).

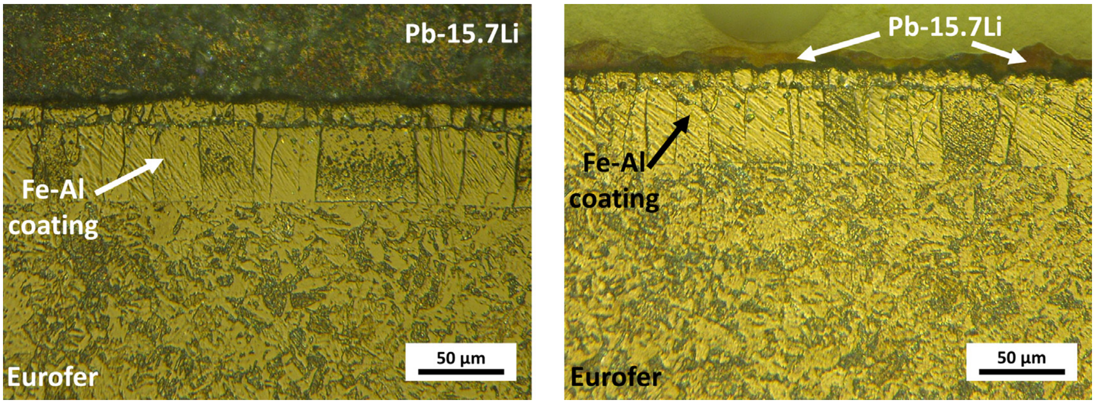

Fig. 4. Cross-sections of ECX coated Eurofer samples after different exposure times in flowing Pb–15.7Li (0.1 m/s; 550 °C): 6026 h (left) and 10,022 h (right) at higher magnification.

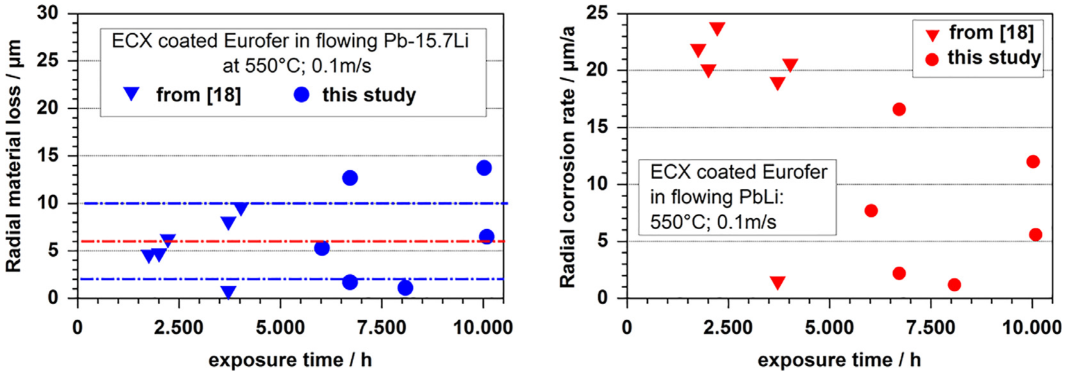

Fig. 5. Radial material loss (left) and corrosion rates (right) of ECX coated Eurofer test samples in dependence on exposure time to flowing Pb–15.7Li.

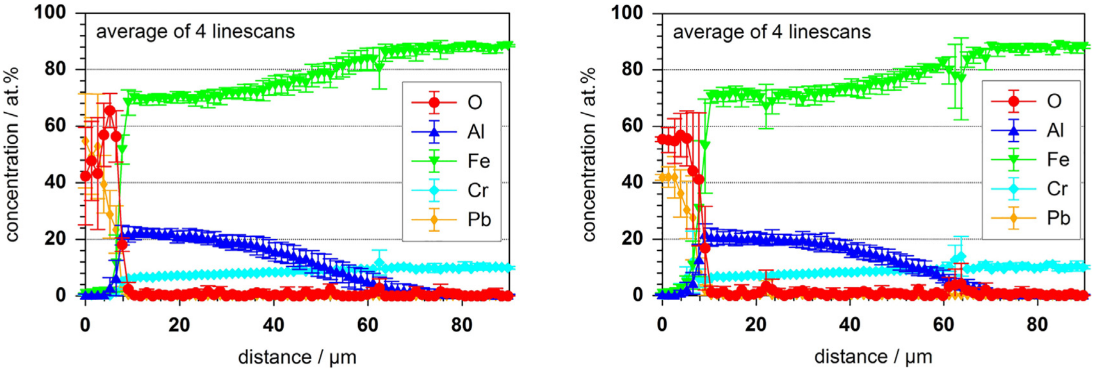

Fig. 6. Average EDS line scans of the cross-sections of ECX coated Eurofer samples after exposure times of 6026 h and 10,022 h in flowing Pb–15.7Li at 550 °C.

half the values estimated after the short-term exposure [18]. This is mainly due to the rather constant radial material loss measured at all exposure times. A similar behavior was observed for the long-term corrosion behavior of ECA coated Eurofer samples in flowing Pb-15.7-Li in the past [15].

3.2. Microstructure after the long-term exposure to Pb–15.7Li

As depicted in the light microscopic images of etched cross-sections in Fig. 4, the observed microstructures of the coatings were similar to cross-sections after shorter exposure times (< 4000 h) as published in [18]. The large columnar grains of the Fe–Al/Fe(α) layer and the underlying typical RAFM / Eurofer microstructure could be clearly identified. In SEM/EDS analyses, the observed sharp boundary between coating and Eurofer matrix corresponded to the point when aluminum is detectable in the EDS line scans. In principle, the average EDS line scans that are depicted in Fig. 6 (see also Section 2.3), showed the typical slopes of decreasing aluminum concentrations in dependence on the distance from the surface. The recorded slopes after long-term exposure of ECX coatings were comparable to reported ones after short exposure to flowing Pb–15.7Li [18]. Derived from the average EDS line scans, the overall coating thicknesses were above 50 µm for all samples, which corresponded to values obtained with the optical microscope.

3.3. Comparison of the long-term corrosion behavior of ECA and ECX coated and bare Eurofer

As the applied experimental conditions i.e. test temperature 550 °C and a flow velocity of 0.1 m/s were similar to previous corrosion test campaigns in PICOLO loop, the corrosion data can be compared to published data for long-term corrosion experiments with ECA coated Eurofer and bare RAFM steels such as Eurofer. Fig. 7 shows the

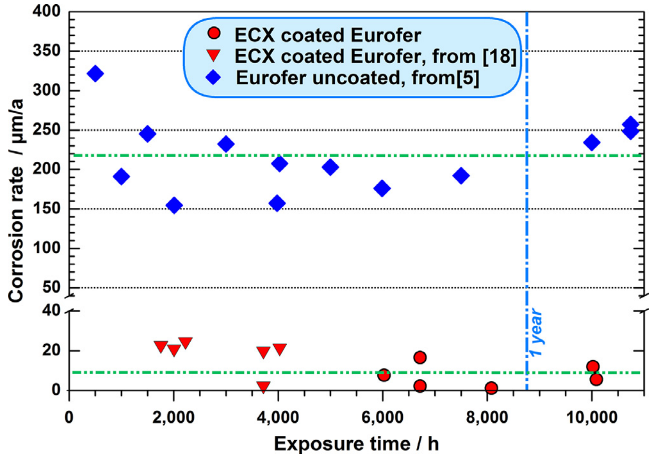

Fig. 7. Comparison of the evaluated radial corrosion rates of ECX coated and bare Eurofer steel tested under the similar conditions in flowing Pb–15.7Li (550 °C, 0.1 m/s).

corrosion rates of bare Eurofer as reported by Konys et al. [5] and ECX coated Eurofer in dependence on exposure time. The short-term data of the ECX coatings with exposure times up to 4000 h was previously published in [18]. Obviously, the corrosion rates could be reduced by applying aluminum-based coatings with the ECX process in comparison to bare Eurofer steel tested under the same conditions. In case of samples that underwent long-term exposure of over 6000 h the corrosion rates were reduced by a factor of up to 20.

When comparing the corrosion behavior of coatings made by ECA [15] and ECX process [18, this study], differences in the corrosion behavior could be observed. As reported by Krauss et al., ECA coatings showed an inhomogeneous corrosion behavior of the Al-based coatings after long-term exposure experiments in flowing Pb–15.7Li [15] and the average corrosion rates of ECA coated Eurofer ranged from about 30 µm/a to 12.5 µm/a after approx. 6000 h and 10,000 h, respectively. In contrast, a reduction of corrosion rate by a factor 1.5 to 3 was observed for Al-based coatings made by ECX process in the current study. This difference confirms the deviations in the corrosion rates between coatings made by ECA and ECX process after short-term experiments (< 4000 h) as reported in [18]: Corrosion rates for ECX coatings were 2 times lower than for ECA coatings. Probably the improved surface quality of the ECX coatings after the electrodeposition of Al and also after the three-step heat treatment was the reason for this improvement in the corrosion behavior [16,18].

4. Conclusion

Long-term corrosion experiments in flowing Pb–15.7Li under fusion relevant conditions (550 °C, 0.1 m/s), revealed a high corrosion resistance of aluminum-based coatings made by the ECX process even for exposure times of up to 10,000 h. The evaluated mean corrosion rates for long-term exposed samples were about or even below 10 µm/a. This implied a reduction in corrosion rate after long-term exposure by a factor of up to 20 compared to bare Eurofer and even a significant reduction with respect to ECA coated Eurofer was determined. In addition, the surface structure of the aluminum-based coatings fabricated by ECX process remained smooth and homogeneous after the exposure; in contrast to the inhomogeneous long-term corrosion behavior of ECA coated Eurofer observed in the past.

This encouraging outcome of this study shows the potential of the electrochemical ECX process based on the electrodeposition of aluminum from ionic liquids. The advantageous corrosion properties promise a significant reduction of precipitation risks in liquid breeder blanket systems and a reliable operation in the future.

Nevertheless, more data and research is needed not only on T/D permeation and thermal cycling behavior of aluminum-based coatings made by the ECX process but also on the observed scattering of the material losses that suggest small deviations in the fabrication, presumably during the mandatory heat treatment procedure.

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