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

Sven-Erik Wulf*, Wolfgang Krauss, Jürgen Konys

Karlsruhe Institute of Technology (KIT), Institute for Applied Materials, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

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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

* Corresponding author.
E-mail address: sven-erik.wulf@kit.edu (S.-E. Wulf).

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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).

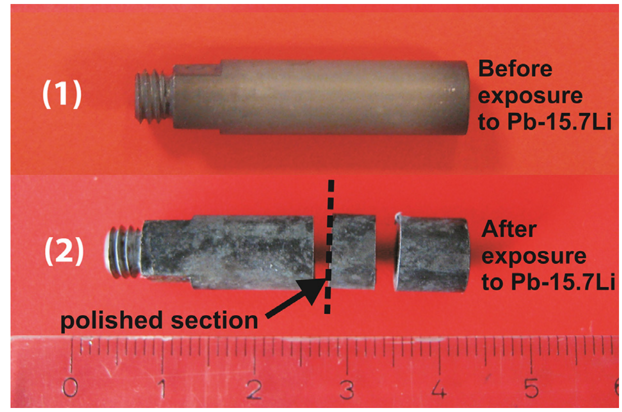

Fig. 2. Appearance of a ECX coated corrosion test sample prior (1) and a long-term exposed sample after cutting (2) prior to the metallographic preparation.

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.

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