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Impact of pretreatment conditions on defect formation during the fabrication of Al-based corrosion barriers by ECX process

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Different breeding blanket designs for DEMO consider Eurofer steel as a main structural material. Nevertheless, RAFM steels suffer from severe corrosion attack if exposed to flowing Pb-15.7Li at high temperatures, as it is considered in the blanket designs HCLL, WCLL and DCLL. Two electroplating processes, i.e. ECA and ECX, were developed in the past to produce protective Al-based coatings on RAFM steels which proved already corrosion protection behavior in flowing Pb-15.7Li under fusion relevant conditions.
Both electrochemical processes need reliable pretreatment processes of the RAFM substrates prior to the Al-deposition, to prevent coating defects such as insufficient covering and weak adhesion. These coating failures increase the risk of defects in the corrosion barriers after the heat treatment and therefore may promote early coating breakdowns in flowing Pb-15.7Li. This study examined some influences on defect formation by electrochemical measurements and SEM/BSE examinations. Besides storage time between mechanical preparation of the samples and electrodeposition, the impact of an anodic pretreatment of Eurofer samples prior to the Al-plating by ECX process was investigated. It is shown that the covering of Eurofer samples by aluminum depend on both parameters and optimized pretreatment parameters could be derived from these findings to increase the reliability of the whole barrier fabrication process.

Keywords: Electrodeposition, aluminum based coatings, Eurofer, pretreatment, ionic liquids, anodic polarization

1. Introduction

Reduced activation ferritic martensitic (RAFM) steels e.g. Eurofer, are considered as structural materials in the construction of different types of breeding blankets for application in DEMO and also in test blanket modules (TBM) tested in ITER [1,2]. Some of the considered blanket designs e.g. HCLL, WCLL and DCLL use the liquid metal alloy Pb-15.7Li as breeding material [2]. In these designs the Eurofer steel components will be exposed to flowing Pb-15.7Li while designated temperatures lay in the range between 300 and 550°C [2]. However, it was shown by Konys et al. that RAFM steels directly exposed to flowing Pb-15.7Li at high temperatures up to 550°C suffer from severe corrosion attack depending on the flow rate, e.g. corrosion rates of around 220 µm per year are reported for Eurofer and CLAM steel at a flow rate of 0.1 m/s and an operating temperature of 550°C [3]. Even higher corrosion rates of up to 400 µm are reported for Eurofer steel at flow velocities of 0.22 m/s [4]. To prevent serious safety risks e.g. tube plugging, due to dissolution, accumulation and precipitation of corrosion products inside of a Pb-15.7Li loop [5], aluminum-based corrosion barriers on RAFM steels were developed in the past [7-9]. Besides hot-dip aluminization (HDA) [9], two electroplating processes i.e. ECA and ECX were developed to coat Eurofer steel with aluminum based layers. These electroplated Al coatings exhibited some advantages compared to coatings made by HDA process; especially during the mandatory subsequent heat treatment in which the protecting aluminum-based barriers are formed [10,11]. Barrier coatings fabricated by HDA and the two electrochemical processes already proved their ability to protect Eurofer from corrosion. Especially, barrier coatings made via electrodeposition of aluminum reduced corrosion rates significantly by a factor of 10. Reported corrosion rates at 550°C and a flow velocity of Pb-15.7Li of 0.1 m/s lay around 20 µm per year at exposure times of up to 12,000 hours in case of ECA process [12] and 4,000 hours in case of ECX process [13], respectively.

However, pretreatment of steel substrates and RAFM steels in particular prior to Al deposition from ionic liquids, as in the case of ECX process, is only rarely documented in literature so far. Especially, with respect to a possible transfer to an industrial process, reliable pretreatment solutions have to be identified. In plating industry water-based pretreatment processes are well established, including degreasing processes and acidic pickling processes to activate the substrate´s surface directly before the electroplating step [11]. The ECX process uses an ionic liquid for Al deposition and therefore it requires a water-free plating environment instead. Thus, the use of water-based reagents is limited because surfaces would have to be dried before the transfer to the dry environment and immersion to the ionic liquid plating electrolyte to avoid unwanted reactions with the electrolyte [12]. Therefore, activation prior to the electrodeposition is still an issue. However, literature data on this is very scarce but some hints are given, that future industrial pretreatment processes could be divided between processes outside the mandatory protective environment e.g. grinding and the degreasing, where standard industrial processes could be used, and

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the activation of the metal surfaces inside a glove box. Besides plasma treatment, anodic polarization seems a promising way to activate steel substrates prior to aluminum electrodeposition from ionic liquids [15-17]. However, the database on this issue is still ambiguous and rare; especially with respect to RAFM steel substrates. Therefore, this study focuses on the possible benefits of an anodic pretreatment and its influence on the quality of the aluminum coating and therefore on the quality of the corrosion barriers after the mandatory heat treatment. Additionally the influence of the pre-plating period (PPP) between the conventional sample preparation by degreasing in a water-based solution and the electroplating inside of a glove box was investigated.

2. Experimental

2.1 Sample preparation and storage

Eurofer samples with a dimension of 15 x 15 mm were cut by Electric Discharge Machining (EDM) from 1.5 mm thick Eurofer steel plate. The samples were roughly grinded towards a thickness of 1 mm, whereby the rolling skin on the steel was removed. Afterwards the surface was grinded with 500 and 1000 grade SiC emery paper, to achieve reproducible technical surfaces prior to the electrochemical experiments (anodic pretreatment / pulse plating). To remove all extrinsic adherent material from the metal surface, e.g. debris from grinding, grease from handling the samples were electrolytically cleaned in an industrial degreasing solution (GALVAROL®, Blendl GmbH Plating Products) containing potassium hydroxide and metasilicate. The degreasing was performed at 40°C and a cell voltage of 3V was applied for 45s. After the degreasing step, the samples were rinsed in deionized water and ethanol and were dried. The backside was covered by chemically resistant adhesive tape. The prepared samples for the investigation of the influence of the length of the pre-plating period (PPP) were stored for 1 to 3 weeks in an exsiccator at a relative humidity of below 1 % under air.

2.2 Electrochemical procedures

Samples were transferred to a glove box after a distinct storage time in the dried air. Inside the glove box the electrochemical pretreatment and the electrodeposition were performed.

Measurement of open circuit potential (OCP) and anodic pretreatment (AP)

For the electrochemical pretreatment and Al deposition a standard three-electrode setup was used with the Eurofer sample acting as working electrode (WE), Al-foil (area 16 cm², *Puratronic 99.998%*, Fa. Alfa Aesar) as counter electrode (CE) and an Al-wire (diameter: 1 mm, *Puratronic 99.998%*, Fa. Alfa Aesar) as quasi-reference electrode (REF). The distance between WE and CE was approx. 50 mm.

The electrolyte used for the anodic pretreatment and the aluminum deposition was a mixture of the ionic liquid 1 - ethyl-3-methyl imidazolium chloride and aluminum chloride which is the same as previously used for electrodeposition of Al by ECX process for preparing Al-based barriers coatings on corrosion test samples [15]. The electrolyte volume in this study was approx. 500 ml and the temperature was 100°C. After the immersion of the samples into the electrolyte the OCP was measured for 60 s. Immediately after the OCP measurement either the anodic pretreatment was started by applying a current density of 10 mA/cm² for 45s or the pulse plating was started in case of specimens without further pretreatment. Figure 1 shows the scheme of the applied current density during the entire experiment.

Aluminum deposition by using pulse plating

Directly after the OCP measurement or the anodic treatment the aluminum deposition was started, respectively.

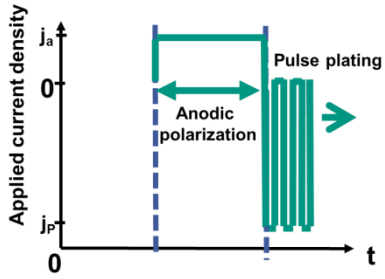

Fig. 1: Scheme of the current density progression during OCP measurement, anodic polarization and subsequent Al electrodeposition.

Thereby, pulse plating was used with following parameters: pulse current densities j_p was 35 mA/cm², t_{on} = 0.5s and t_{off} = 0.5s, leading to a mean current density j_m of 17.5 mA/cm². The number of applied pulse cycles was usually 2070. Figure 2 shows the plot of the applied current and measured potential vs. REF in the initial phase of the pulse plating procedure at an anodically activated Eurofer surface. After the electrochemical experiments the samples were rinsed in ethanol and acetone.

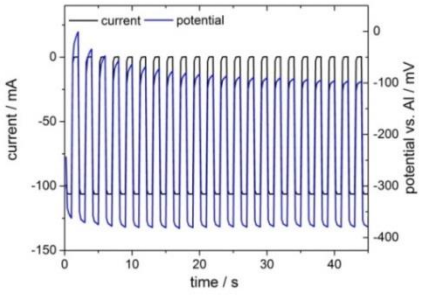

Fig 2: Plot of applied current and measured potential vs. time in the initial phase of the pulse plating procedure at an anodically activated Eurofer surface.

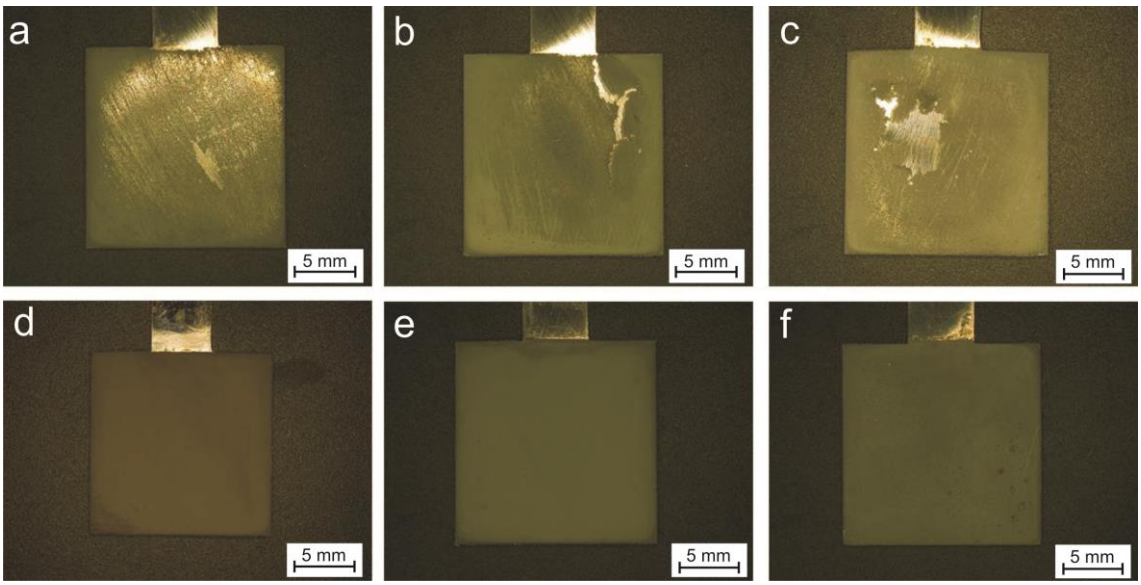

Figure 3: Light microscopy images of ECX coated Eurofer without (upper row) and with anodic pretreatment (lower row) in dependence on the pre-plating period: PPP approx. 1-2 h (a,d), PPP = 1 week (b,e) and PPP =3 (c,f).

2.3 Post experimental characterization

After the experiments, the samples were examined by using light and scanning electron microscopy (SEM). In the SEM additionally the back scattered electron (BSE) imaging mode was used to determine failures in the Al coating by observing contrast differences between the coating i.e. dark color and areas with failures that appears bright in the BSE images due to the higher ordering numbers of the chemical elements of the Eurofer steel substrate.

3. Results and discussion

3.1 Influence of anodic pretreatment

Figure 3(a-c) illustrates the typical appearance of Al coated samples with and without anodic pretreatment for 45s. Samples without further anodic treatment exhibited large uncoated areas. If these coatings would be further processed, these areas would lead to failures in the Fe-Al coatings with no corrosion properties at these local areas. Additionally, in case of samples with a pre-plating period of above 1 week poor adhesion to the substrate was observed which led to partial delamination of the Al coating during the rinsing procedure after the electrodeposition.

The potential vs. time plots during the open circuit potential measurement, as given in figure 4, showed clearly a dependence of the OCP on the pre-plating period. Thereby the measured average OCP range was between 590 mV vs. Al in case of the freshly prepared samples and 650 mV in case of samples with long PPP of 2 and 3 weeks. This indicates that the Eurofer surface becomes "less" active due to natural oxide formation in dependence on storage time. This could explain the poor aluminum adhesion to the Eurofer substrates for stored samples without anodic pretreatment. However, even in the case of the freshly prepared samples some surface

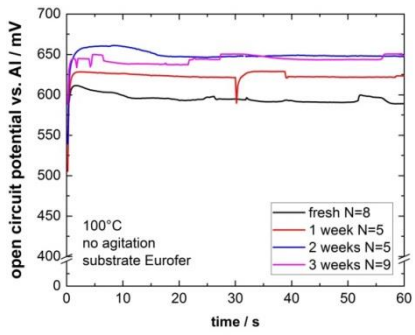

Figure 4: Average OCP vs. time plots measured on Eurofer steel substrates in dependence on the pre-plating period.

areas "passivated" during the transfer into the glove box, leading to extended areas of uncoated Eurofer.

In contrast to this, all samples pre-treated for 45s by anodic polarization where covered by an aluminum coating without macroscopic defects and good adhesion to the substrate, i.e. no delamination of the coatings occurred, see figure 3 (d-f). This is a good indication for the capability of the anodic polarization to remove most of the thin natural oxide layer and activate the Eurofer surfaces sufficiently prior to the electrodeposition.

3.2 Influence of pre-plating period

When repeating the experiments with the anodic pretreatment 3-4 times for each PPP it appears, that the probability of observing microscopic failures, i.e. small uncoated areas in range of some µm to 60 µm in diameter, rises with increasing PPP.

In case of freshly prepared samples a good reproducibility was achieved with the applied anodic

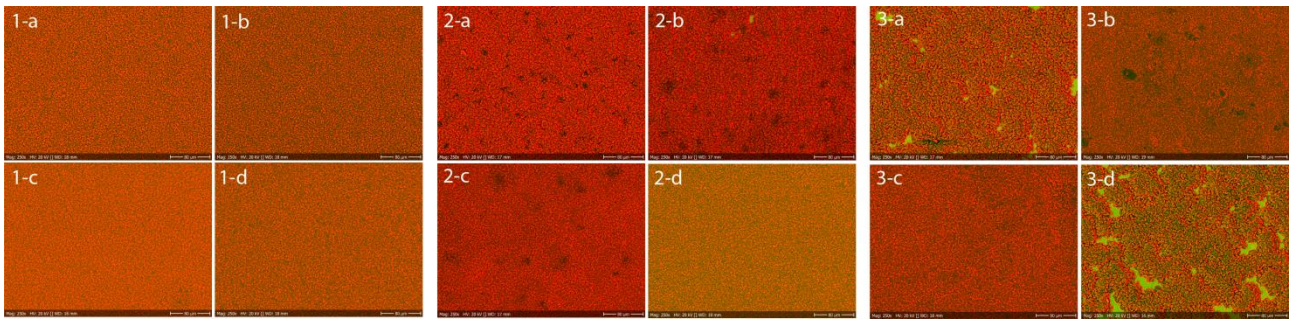

Figure 5: Merged SEM and BSE images of different electroplated Al coatings on anodically pretreated Eurofer substrates in dependence on the pre-plating period: 1 a-d- freshly prepared, 2 a-d - after PPP = 1 week and 3 a-d - PPP = 2 weeks (right).

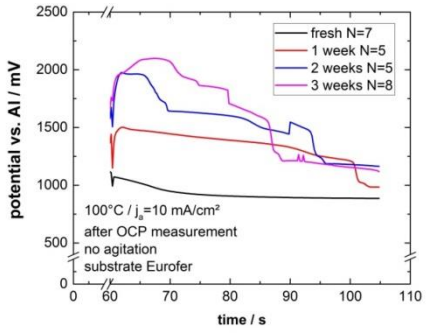

Figure 6: Potential vs. time plots during the anodic polarization in dependence on the PPP.

pretreatment and no failures were observed by SEM/BSE examinations, see figure 5. An acceptable reproducibility was also observed in the replicate tests for a PPP of one week and only very few small failures were observed at one sample (figure 5, sample 2-b). Despite the anodic pretreatment for 45s, the probability of failures increased when the PPP exceeded 1 week and the reproducibility decreases obviously, as it is depicted for PPP of 2 weeks in figure 5. This finding indicates that the activation of the Eurofer substrates was not sufficient and the natural oxide layer was not removed completely during the 45s of anodic treatment.

These obvious differences in the activation behavior of the Eurofer substrates depending on the PPP could be observed in the potential vs. time measurements during the anodic polarization procedure, as shown in figure 6. In case of the freshly prepared samples the anodic dissolution of the substrate started more or less instantly after the anodic current was applied and continued for the whole duration of the pretreatment. For a PPP of 1 week the potential is higher due to a higher resistance against the dissolution, evoking from the thin natural oxide layer in the beginning. However, at the end of the pretreatment the measured potentials are in the same range as for the freshly prepared samples, indicating a completely active surface. The two other average slopes represent PPP´s above 1 week. It could be observed that high potentials of up to 2 V vs. Al occurred in the beginning of the pretreatment, which is due to thicker natural oxides on the surface. After reaching the maximum, that correspond to the onset of local dissolution of Eurofer, the potential decreases but the average potentials do not reach the low values of the average E-t slopes as in the case of short PPP´s, suggesting that inactive areas are still present after 45s of anodic pretreatment. This indicates that the duration of the pretreatment procedure of 45s is too short for a sufficient activation in case of long PPP´s.

4. Conclusion

Corrosion barriers on Eurofer steel made by electrochemical Al deposition processes such as ECX and a subsequent heat treatment are considered for applications in breeding blankets with liquid Pb-15.7Li. To transfer these fabrication processes to a post-laboratory scale all process steps, i.e. electrodeposition and heat treatment, have to ensure good reliability and have to be adapted to industrial procedures. With respect to this, especially the pretreatment prior to the electrodeposition on Eurofer substrates plays a major role because the achievable qualities of the final Al-based corrosion barriers depend strongly on the reliability of the electroplating step on Eurofer substrates.

Therefore, this study elaborates anodic polarization as one possible route to pretreat Eurofer steel samples directly before the electrodeposition. It was shown that a single basic pretreatment by grinding and degreasing is not sufficient to achieve aluminum coatings with good reliability with respect to the adhesion to the substrate and low failure density on Eurofer steel. In contrast, the introduction of an additional pretreatment step by anodic polarization to activate the steels surface immediately prior to the electrodeposition of aluminum strongly increases the reliability of the coating quality. Besides this it was shown that the pre-plating period between the conventional samples preparation e.g. grinding, degreasing and the activation step had an impact on failure occurrence. Thereby, PPP of below 1 week seemed to be acceptable when applying 45s of anodization. This indicates that sample preparation and the activation/electrodeposition steps could be divided in the future industrial applications. This finding has to be considered during any future upscaling of the ECX process, to coat larger components made of Eurofer.

An additional outcome of this study was that potential measurement during the anodic polarization showed good a correlation with the coating quality, indicating a

promising way to increase the reliability of the whole ECX process in the future.

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