Development of Electrochemical Processes for Aluminium-Based Coatings for Fusion Applications

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Reduced activation ferritic-martensitic steels (RAFM) are envisaged in future fusion technology as structural material which will be in direct contact with a flowing liquid lead-lithium melt, serving as breeder material. Aluminium-based coatings had proven their ability to protect the structural material from corrosion attack in flowing Pb-15.7Li and to reduce tritium permeation into the coolant, significantly. Coming from scales produced by hot dipping aluminization (HDA), the development of electrochemical-based processes to produce well-defined aluminium-based coatings on RAFM steels gained increased attention in research during the last years. Two different electrochemical processes are described in this paper: The first one, referred to as ECA, is based on the electrodeposition of aluminium from volatile, metal-organic electrolytes. The other process called ECX is based on ionic liquids. All three processes exhibit specific characteristics, for example in the field of processability, control of coating thicknesses (low activation criteria) and heat treatment behavior. The aim of this article is to compare these different coating processes critically, whereby the focus is on the comparison of ECA and ECX processes. New results for ECX will be presented and occurring development needs for the future will be discussed.

Keywords : *Al-based coating, corrosion barrier, tritium permeation barrier, ionic liquids*

1. Introduction

Steel structures made of reduced activation ferritic martensitic steels (RAFM-steels) are proposed for application within the blanket system of a future fusion reactor. This claims development of suitable steels, functional scales and the qualification of them to fit the desired requirements in such challenging environments.

In the proposed HCLL (helium-cooled lead lithium) concept for a future fusion reactor, the envisaged breeding material is a flowing, liquid Pb-15.7Li melt, which has direct contact to the desired structural steel. The envisaged operating temperatures in this concept lie above 480 °C and reach in some designs 550 °C. Under these conditions bare RAFM-steels such as Eurofer97, Optifer IVa, Manet I and F82H-mod. suffer from uniform but significant corrosion attack[1,2]. For example Konys et al. reported relatively dramatic dissolution rates of Eurofer97 of about 400 μm per year at operation temperatures of 550 °C and a Pb-15.7Li flow rate of 0.22 m/s[3]. To enhance the performance limits of such steels, the application of functional coatings is essential for the realization of a future blanket system. Coatings on RAFM-steels are envisaged to provide (a) reduced tritium permeation rates through the structural material and (b) corrosion protection properties, in contact with the liquid breeder material Pb-15.7Li[4]. To fulfill these requirements in Pb-Li systems, aluminium-based coatings on RAFM steels seem to be advantageous since they are able to offer both properties at once. Thereby, the formation of an Al$_2$O$_3$ layer acts as a barrier on the surface of aluminium-rich coatings to provide reduced tritium permeation rates[5]. The ability of aluminium-rich coatings to reduce corrosion rates of RAFM steels in flowing Pb-Li melts compared to the bare steel material, were shown in studies by Glasbrenner et al.[6], and Konys et al.[7], for operating temperatures between 480 °C and 550 °C and flow rates up to 0.3 m/s.

Several coating processes were under more or less intensive investigation to produce the desired aluminium-rich scales on RAFM steels. Each technique possesses inherent advantages and disadvantages with respect to plating rates, thickness distribution, coatings of different geometries, scale formation, expenses and stability in the Pb-15.7Li environment. Besides chemical vapor deposition (CVD) and vacuum plasma spraying (VPS)[8], main research was focused on the hot dip aluminizing process

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Table 1. Comparison of electrochemical Al deposition processes ECA and ECX

	ECA	ECX
Al source	$NaF\text{-}Al(C_nH_{2n+1})_3$	$AlCl_3$
Electrolyte	e.g. toluene-based	[Emim]Cl, [Bmim]Cl
Operating temperature	95 °C – 103 °C	< 100 °C
Current desity	10 mA/cm^2	10-20 mA/cm^2
Current efficiency	Ca. 100 %	Ca. 100 %
Deposition rates	12 μm/hour	25 μm/hour
Pulse-plating	Yes [18]	Yes[15-17]
Vapor pressure of system	High	Very low
Inflammability/Sensitivity	High/Sensitive to oxygen and hydrogen	Low/Sensitive to humidity

(HDA) to produce Fe-Al scales on RAFM steels, in the beginning of these research activity[6,7,9].

Meanwhile, different electrochemical based processes with their specific advantages were introduced in the field of fusion technology and are still under intensive investigation. They seem to be an interesting new alternative to produce aluminium-based barriers for blanket applications[4,10] which additionally promise better technological and industrial relevance. The present paper describes these electrochemical processes developed at KIT in more detail and presents scales produced electrochemically. The results are discussed in respect to scales produced by the HDA process in the past.

2. Aluminization Processes

2.1 Hot-dip aluminization

In the hot-dip aluminization process (HDA), the parts to be plated are immersed into a melt of aluminium (e.g. T=700 °C) for a certain time, whereby short dipping times of 30 s are to be favored ensuring complete wetting of the steel parts but also minimizing the amounts of aluminium reacting with the steel (low activation criteria). Afterwards the plated parts are removed from the Al melt and cooled naturally[1,8]. Besides an aluminium layer on top of the sample, an aluminium-rich reacting zone consisting of mostly brittle Fe_2Al_5 phase is formed on the substrate material, e.g., RAFM steel, due to relatively high temperatures of the melt[8]. The conversion to suitable barriers is done by performing a heat treatment subsequently.

2.2 Aluminization by electroplating

2.2.1 General electroplating

Compared to other plating techniques such as hot-dip metallization or CVD, electrochemical metal deposition in general provides some favourable properties:

- Good controllability of layer thickness, from nanometer to millimeter scale by controlling current density and time (*Faradays law*).
- Thickness distribution is controllable by choosing special shaped anodes and/or adjusted deposition parameters (current density (j), pulse-plating) à complex shaped parts could be plated.
- Low temperature process (e.g., <100 °C) à low energy consumption

Another advantage is the long history of commercialized plating processes and a long experience for plating different metals on a variety of substrates.

However, these well described processes are mainly based on aqueous electrolytes, and therefore reached some limitations in the past. For example, the plating of hydrogen sensitive materials, such as high strength steels, is difficult and the deposition of and on highly electronegative metals is impossible due to hydrogen evolution during the plating process or incomplete reduction to metallic state. To overcome these limitations new classes of water-free electrolytes are under development to introduce electrochemical processes with their advantages to new technological applications, such as electrochemical aluminium deposition which was possible earlier only from high temperature molten salts.

2.2.2 Electrochemical deposition of aluminium

Due to its very negative standard potential of about -1.7 V vs. NHE (normal hydrogen electrode), aluminium plating from water-based electrolytes, is not possible[11]. Therefore, non-aqueous electrolytes are required for aluminium electrodeposition. Besides the electrodeposition from molten salts, different low temperature electrodeposition processes (<100 °C) were developed in the past.

The former process, referred to as ECA (electrochemical deposition of aluminium from organic aprotic electrolytes) process is an commercialized plating process, based on
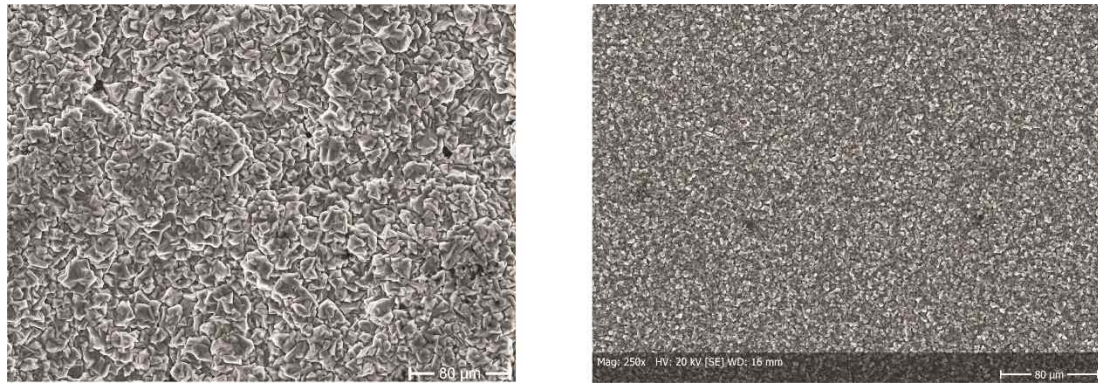
Fig. 1. SEM images of surfaces of electroplated Al layer (20 μm thick) on Eurofer steel: ECA process – 10 mA/cm² (left) and ECX process – 20 mA/cm² (right).

metal-organic electrolytes where Al-alkyl compounds (as aluminium source) are dissolved in a volatile organic solvent, e.g. toluene[10-12]. Due to the use of highly volatile solvents and highly water sensitive organo aluminium, the plating process has to be done in a very good protective environment.

A second, more recent plating process referred to as ECX (electrochemical deposition of aluminium from ionic liquids containing metal salt) in the field of fusion technology is based on ionic liquids (IL). This is a relatively new class of electrolytes that gained a lot of attention in the field of metal deposition during the last decade[13]. Ionic liquids are defined as ionic compounds that are liquid at temperatures below or around 100 °C. Electrodeposition of aluminium from such electrolytes mainly based on eutectic mixtures of an imidazolium-type IL and AlCl₃ as metal source, whereof 1-ethyl-3-metyhlimidazolium chloride ([Emim]Cl) and 1-ethyl-3-butylimidazolium chloride [Bmim]Cl are the most commonly used ILs for aluminium deposition[14,15]. The main process parameters and properties for ECA and ECX process are summarized and compared in Table 1.

In the last years, both electrochemical processes were under investigation in fusion technology to produce tritium-permeation and corrosion barriers on RAFM steels by electrochemical methods. Thereby, adherent aluminium coatings on RAFM steels, e.g. Eurofer (European 9 % Cr-steel) were achieved by both processes[10,16]. Since the current density limits are higher in the case of ECX, pulse plating can be used in a wider extend then in the case of ECA, and therefore smoother and finer grained coatings could be achieved by the ECX.

Fig. 1 compares surfaces of Al layers of approximately 20 μm thickness on Eurofer steel after electrochemical plating by ECA (Fig. 1 left) and ECX (Fig. 1 right) process, whereby the Al surfaces produced by ECX exhibit

significant crystallites presumably due to the possibility of pulse-plating.

XRD spectra measured at these surfaces revealed that pure, crystalline aluminium coatings are achieved by ECA and ECX processes (see Fig. 2). The (111), (200) and (220) peaks measured at the 20 μm thick coatings are characteristic peaks for metallic Al, whereby the latter ones are more pronounced in the case of the ECX coating, indicating the existence of different crystallographic orientations.

Another consequence of limited current densities in the case of ECA is that the maximum deposition rates of the ECA process are lower compared to the ECX process. Fig. 3 shows cross sections of Al coatings with similar thickness, for both processes, illustrating the higher deposition rates achieved by ECX process. Furthermore, the pictures show that ECX produces smoother layers compared to Al-layers made by ECA process.
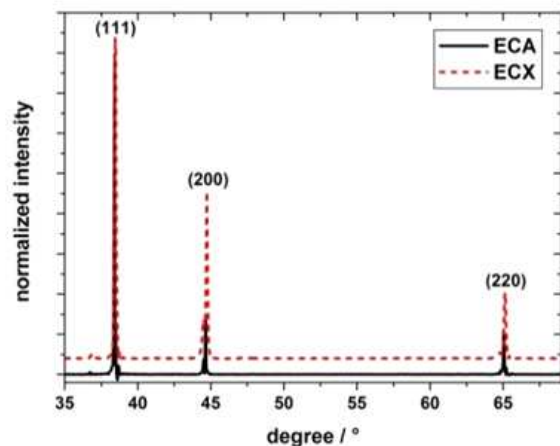

Fig. 2. XRD spectra of electrodeposited 20 μm thick Al coatings made by ECA and ECX (dotted line) process.

Table 2. Heat treatment parameters for steels, aluminized by HDA, ECA and ECX processes

	Step 1	Step 2	Step 3	Substrate steel	Reference
HDA	-	1040- 1075 °C/0.5 h	750 °C/1-2 h	MANET II, F82Hmod.	8,20-22)
	-	980 °C/0.5 h	760 °C/1.5 h	EUROFER	7)
ECA	-	980 °C/0.5 h	760 °C/1.5 h	EUROFER	10)
ECA/ECX	640 °C / 4 h	980 °C/0.5 h	760 °C/1.5 h	EUROFER	16,19)
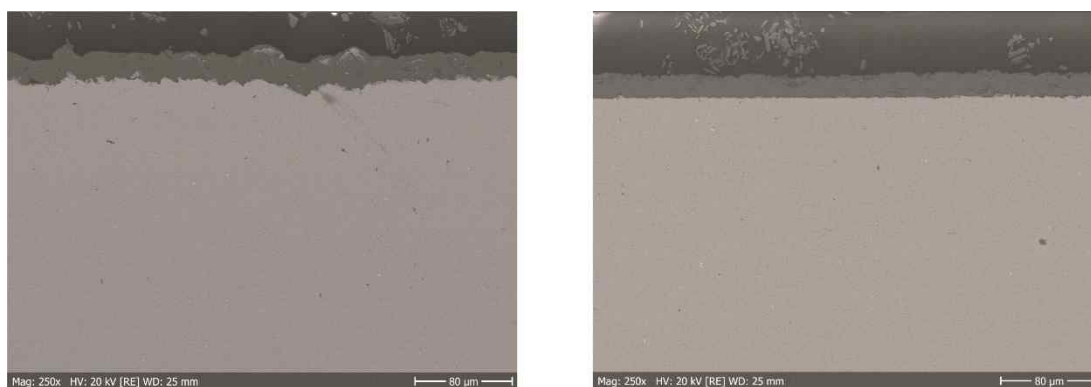
Fig. 3. Cross sections of electroplated Al layers (20 μm) on Eurofer: ECA process - 10 mA/cm² t = 2h (left) and ECX process - 20 mA/cm², t = 1h (right).
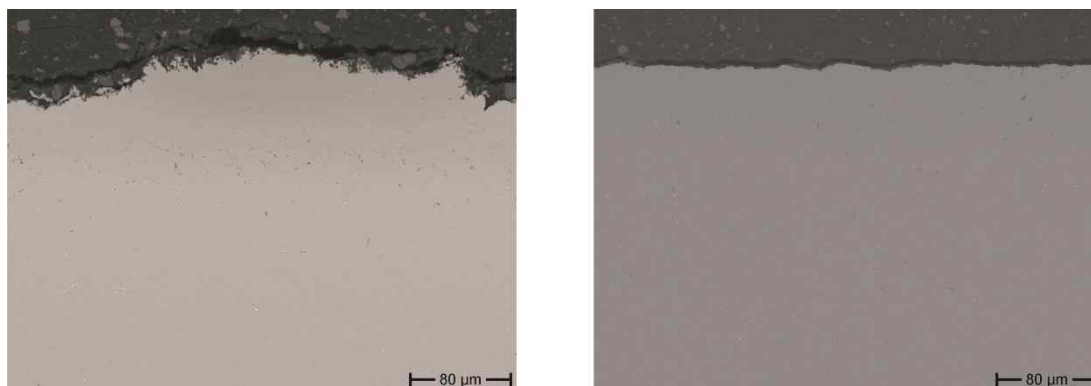
Fig. 4. Cross sections of Fe-Al scales on Eurofer after HT (640 °C, 4 h; 980 °C, 0.5 h and 760 °C, 1.5 h): ECA (left), ECX (right).

3. Heat Treatment

Independently from the aluminization process (HDA, ECA or ECX), the aluminized steel parts have to be heat treated to form the desired ductile Fe-Al scales on RAFM steels supposed to act as barriers in a future fusion reactor. Without heat treatment, the highly soluble Al would be immediately dissolved in the liquid PbLi alloy. Typical heat treatment conditions for aluminized steel parts are shown in Table 2.

3.3 Heat Treatment of HDA-plated Steel Substrates

In the case of HDA coated low activation steel, the subsequent heat treatment process has to convert the brittle Fe_2Al_5 phase and adherent pure Al layer into softer phases and an Al_2O_3 surface scale. The heat treatment consisted of a two-step process, a high and a low temperature step to keep the ferritic-martensitic (FM) structure unchanged (see Table 2). For MANET II, F82H-mod. and Eurofer steels (all are 9% Cr-steels at different stages of development) it was shown, that the brittle phases are transformed

into FeAl and α-Fe(Al) phases. The overall thickness of the reacted scale on low activation steels has been reported to vary between 150 μm[7,19] and 250 μm[8]. Using standard heat treating conditions (standard pressure), it was found, that a dense band of pores occurred inside the transformed scale[8,22] after the heat treatment process. These pores are supposed to be Kirkendall pores resulting from long diffusion distances, due to thick Fe_2Al_5 phase and different diffusion coefficients of Al and Fe in the steel. These pores can be suppressed by heat treating the aluminized steel samples under superimposed pressure conditions[22,23]. Unfortunately, the application of very high pressures (>1000 bar) can lead to crack formation in the area near to of the processed scales[22].

3.2 Heat Treatment of electroplated Al-layers

In case of the electroplated Al-layers on RAFM steels, pure Al has to be converted into the desired ductile Fe-Al phases. First tests used the two-step heat treatment procedure known from HDA examinations and adjusted it to Eurofer steel substrates[10]. This procedure was optimized by Konys et al. to a three-step HT process in the last years, see Table 2[19]. Additionally it was also shown by Wulf et al. that dense and homogenous Al layers are mandatory for a proper transformation of the pure Al into the desired Fe-Al phases[16]. Following these recommendations, electrodeposited Al layers, either produced by ECA or ECX could be transformed into ductile Fe-Al phases, while only very few pores are observable. Cross sections shown in Fig. 4 of heat-treated electroplated 20 μm thick Al coatings on Eurofer steel, revealed comparable results for ECA and ECX plated samples although the surface of the annealed ECA sample seemed to be rougher. EDS line scans after heat treating the electrodeposited Al-layers revealed that in all cases the maximum content of aluminium found in the Fe-Al scales was below 45 at.%, indicating the complete transformation of the pure Al-layer into the desired low aluminium rich Fe-Al phases FeAl and α-Fe(Al). Fig. 5 shows two EDS line scans for the cross sections shown in Fig. 3. It is observable that under the same conditions (20 μm thick pure aluminium, same HT conditions), comparable concentration profiles were achieved for scales produced by ECA and ECX. The maximum extent of the reacting zone after HT was below 90 μm in this case (20 μm Al). The concentration profiles found here are in good agreement with earlier findings for heat-treated Al-layers on Eurofer reported by Krauss et al. (ECA, without 640 °C HT step)[10] and Wulf et al. (ECX, lower Al thickness)[16].

4. Results and Discussion

All three aluminization processes presented here were able to produce aluminium-based coatings on RAFM steels. All three processes have in common, that a subsequent heat treatment is necessary after the actual aluminization of the substrate, whereby the HT of HDA samples requires a specific heat treatment with superimposed pressure to suppress pore formation. Further, in the HDA process the minimum layer thickness is limited and high Al amounts are introduced into the steel surface. Due to an difficult controllability of coating thickness, complex-shaped parts might hardly be coated with an uniform Al-coating by HDA. For example the realization of a uniform thin coating on parts with curves, cavities and edges seems to be challenging or impossible. Electrochemical plating techniques might be an affordable and good adaptable way to overcome these limitations. The electrochemical processes, ECA and ECX offer the possibility to control the Al-layer thickness in the micrometer range which is not achievable by HDA process. Due to the lower achievable Al-layer thickness (lower amounts of aluminium), which is also an important point to fulfill low activation requirements, pore formation could be avoided or minimized at least in the case of electrochemically produced scales. The latter will be essential when testing electrochemically produced scales for their tritium-permeation barrier properties or corrosion resistance. Since both electrochemical processes are suitable to electroplate uniform, dense and homogeneous Al-layers on Eurofer steel and to transform these layers into the desired Fe-Al phases, main differences can be found in the nature of the electroplating process itself.

Since the ECA process is a commercialized process, industrial experience exists for the electrodeposition of
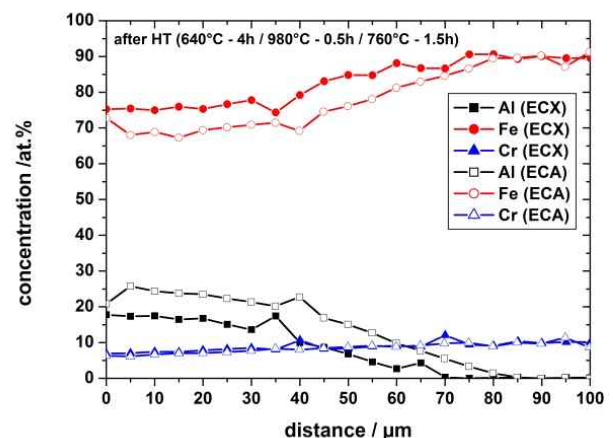

Fig. 5. EDS line scan of Eurofer, coated with 20 μm thick Al by ECA and ECX (filled-out symbols) after heat treatment.

aluminium for many years[11]. The main disadvantages are the relatively high costs, due to complex and expensive equipment needed to fulfill encapsulation and safety requirements for the whole process, lower scattering behavior in plating for complex structures and very important for coating of drills, or less influence on microstructure of deposited layer. This might be also valid issues when adapting this process to complex shaped and large parts and implies drawbacks.

Compared to ECA process, the new developed ECX process showed some favorable advantages. Besides, the use of less dangerous chemicals in the ECX process, that might lead to lower expenses for plating equipment, the deposition parameters (current densities, temperatures, agitation) could be adapted to specific tasks in a wider range as in the case of ECA. For example, the current density range applicable during electrodeposition is wider and provides the possibility to reach higher deposition rates, e.g. in this study the deposition rates achieved for ECX were double the ones for ECA. For the same reason the use of classic pulse plating is possible when using ionic liquids (ECX process), which has been shown by several studies in the last few years[15-17,23]. For the ECA process the use of pulse plating was mentioned only in few papers[18]. Due to the limited current density window applicable during electrodeposition, the use of pulse plating seemed to be limited for the ECA process in the future. However, pulse plating within the ECX process is a promising way to improve and control the properties of electrochemically deposited Al-coatings, such as layer morphology[16], homogeneity, thickness distribution and orientation/crystallinity (this study). Due to the novelty of the ECX process, limited industrial experience exists for this process up to date, compared to ECA.

5. Conclusion

Comparing three aluminization processes envisaged for the production of aluminium-based T-permeation and corrosion barriers for applications in a future fusion reactor, the electrochemical processes, ECA and ECX offer significant advantages to the earlier developed HDA process. These advantages arise from the improved controllability of coating thickness and the ability to deposit thin Al coatings (micrometer range) on RAFM steels, what is preferable concerning low activation criteria and seems to facilitate subsequent heat treatment processes.

Since the properties of scales made by HDA were under intensive investigation, concerning corrosion protection and T-permeation properties, for several years[4-9], such tests are up to date in an initial stage in case of Fe-Al

scales produced by the electrochemical processes, ECA and ECX and have to be intensified in the next years. Beside these important tasks, the actual electrochemical processes need ongoing examination of preferable deposition parameters, concerning thickness distribution and reproducibility or to the issue of surface morphology including aging behavior. Due to the improved flexibility compared to ECA, and therefore the possibility to use pulse plating, the focus will be directed onto the ECX process in the future.

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