Zr-based conversion coatings for multi-metal substrates

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Table of content

Chapter 1: Introduction

1.1. Current state of the art	1
1.2. Aim of the research	2
1.3. Outline	3
1.4. Research approach	4
1.5. References	5

Chapter 2: Initiation and growth of Zr-based conversion coatings on multi-metal surfaces

2.1. Introduction	8
2.2. Experimental	9
2.2.1. Materials and sample preparation	9
2.2.2. Experimental approach	10
2.3. Results and discussion	11
2.3.1. Open circuit potential during the deposition	11
2.3.2. Surface characterization	13
2.4. Conclusions	20
2.5. References	21

Chapter 3: The effect of convection on the formation of Zr-based conversion coatings on multi-metal surfaces

3.1. Introduction	24
3.2. Experimental	25
3.2.1. Materials and sample preparation	25
3.2.2. Experimental approach	26
3.3. Results and discussions	27
3.3.1. Open circuit potential during the deposition of the Zr-based conversion films	27
3.3.2. Ex-situ surface analysis of the Zr-based conversion coatings	31

3.4. Conclusions	35
3.5. References	36

Chapter 4: The influence of surface hydroxyls on the formation of Zr-based conversion coatings on AA6014 aluminium alloy

4.1. Introduction	40	
4.2. Experimental		
4.2.1. Materials and sample preparation		
4.2.2. Surface characterization	42	
4.2.3. Open circuit potential during the deposition of the Zr-based conversion layers	42	
4.3. Results and discussion	43	
4.3.1. Surface chemistry and elemental distribution of the treated samples	43	
4.3.2. Surface chemistry and elemental distribution of Zr-based films deposited on the differently		
treated samples	47	
4.3.3. Open circuit potential evolution during the deposition of Zr-based layers		
4.4. Conclusions	57	
4.5. References	57	

Chapter 5: The effect of surface conditioning treatments on the local composition of Zr-based conversion coatings formed on aluminium alloys

5.1. Introduction	61
5.2. Experimental	63
5.3. Results and discussion	64
5.3.1. FE-AES study of the differently treated AA6014 samples	64
5.3.2. FE-AES study of the Zr-based conversion coatings deposited on the differently	treated
aluminium alloys	68
5.3.3. FE-AES surface morphology study of thermally pre-conditioned AA6014	75
5.4. Conclusions	78
5.5. References	79

Chapter 6: Comparison of the effect of surface hydroxyls on the formation of Zr-based conversion coatings on different metals 6.1. Introduction 82 6.2. Experimental 83 6.2.1. Materials and sample preparation 83 6.2.2. Surface characterization 84 6.2.3. Open circuit potential during the deposition of the Zr-based conversion layers 85 6.3. Results and discussion 85 6.3.1. Surface characterization of the differently treated cold rolled steel samples 85 6.3.2. Surface characterization of the Zr-based conversion coatings formed on the differently treated cold rolled steel samples 87 6.3.3. Open circuit potential evolution during the deposition of Zr-based layers 94 6.4. Conclusions 96

65	References

Chapter 7: General conclusions

7.1. Introduction	100
7.2. Approach	100
7.3. Formation mechanism of Zr-based conversion coatings on different metals	101
7.4. Influence of the surface conditioning treatments on the deposition of Zr-based	conversion
coatings on different metals	103
7.5. Recommendations	104
7.6. References	106
Summary	107
Samenvatting	109
Appendix: Complementary figures	111
Acknowledgements	113
List of publications	116

96

Curriculum Vitae

1. Introduction

1.1. Current state of the art

Conversion coatings are applied on metallic surfaces to promote paint adhesion and improve the corrosion performance. These coatings are generally formed by immersion of the substrate in a bath through an electrochemical driven process without the use of an external current. In the automotive industry, phosphate conversion coatings have been used for many years because they provide an excellent performance for ferrous and non-ferrous alloys [1]. However, the phosphate conversion process has several disadvantages. The phosphate conversion bath typically operates above room temperature, increasing the overall costs of the process. Phosphate coatings often require a post sealing process with chromic acid in order to reduce the porosity of the film [2]. Moreover, this treatment generates a large amount of sludge and the discharges of the conversion bath have a detrimental effect on water resources. An important challenge nowadays is to come up with a suitable replacement for this treatment, able to provide a similar or even better adhesion performance than traditional phosphating treatments. One of the most promising alternatives, is the Zr-based conversion treatment. This process consists of the exposure of the metallic surface to hexafluorozirconic acid solutions, which leads to the formation of a conversion coating mainly composed of ZrO₂ and having a thickness of less than 100 nm [3-5].

Figure 1.1, shows a schematic representation of the different steps involved in the Zr-based conversion treatments. Metal components that will be coated usually present heavily contaminated surfaces. These contaminations originate from the forming process itself and long storage times. Additionally, the surface commonly contains an oil layer which is used to provide temporary corrosion protection. These contaminations must be removed because it hinders a proper formation of the conversion coatings. For that reason, a surface conditioning treatment is commonly applied. After the surface conditioning treatment, the Zr-based conversion coating is applied.

Chapter 1



Figure 1.1: Schematic representation of the different steps in the formation of the Zr-based conversion coatings.

1.2. Aim of the research

Several authors have described the different stages involved in the formation of the Zr-based conversion coatings [6-10]. The first step in the formation of the conversion film is chemical dissolution of the oxide film by the free fluorides present in the conversion bath. The formation of the film starts as a result of an increase in the pH at the metal/solution interface promoted by the hydrogen evolution and oxygen reduction reactions. Since the deposition of the Zr-based conversion coatings is an electrochemically driven process, clear differences in the formation of the films are expected depending on the substrate given the fact that metals such as aluminium, iron and zinc behave complete different in aqueous solution [11-13]. However, a comparison of the deposition process on different substrates has not been reported yet. This is crucial for the automotive industry, because nowadays car bodies are composed of different metals.

Moreover, depending on the surface conditioning treatment parameters prior to the application of the conversion coating, the oxide film might be modified. This change in the oxide might have an important effect on the first step in the formation of the film, and consequently on the surface characteristics of the resulting conversion layer [9]. Therefore, it is important to assess how the surface conditioning treatments affects the formation of the film on different alloys. The main goal of this research was to obtain a better understanding about these two points.

1.3. Outline

This PhD thesis is divided in 7 chapters as outlined in Figure 2. The general introduction and approach are given in Chapter 1. The results and discussion are divided in 5 Chapters. In Chapters 2 and 3, the mechanism of formation and the effect of convection on the formation of Zr-based conversion coatings on different metals are studied in detail. The following three chapters are focused on studying the effect of the surface conditioning treatments on the formation of the Zr-based conversion coatings on different metals. In the last chapter, Chapter 7, the general conclusions of this works are presented.



Figure 1.2: Layout of this PhD thesis.

1.4. Research approach

In this study, a Cu-containing Zr-based conversion solution was used for the deposition of the Zrbased conversion coatings. Different substrates were evaluated thoughout this work; AA6014, cold rolled steel, hot dip galvanized steel and AA1050. Moreover, the results presented by Taheri et al. [14] for the formation of Zr-based conversion coatings on pure zinc were used to establish a comparison for different metals. Figure 1.3 introduces a schematic diagram of the approach used throughout this work. The experimental approach is divided in two parts: In-situ electrochemical analysis and Ex-situ Surface Analysis. Following previous studies in the topic, it is known that the formation of the Zr-based conversion coatings can be studied and analyzed using in-situ electrochemical analysis. This is done by measuring the Open Circuit Potential (OCP) as a function of time when the substrate is immersed in the conversion solution. However, for the interpretation of the results it is required to use one or more complementary techniques [15]. For that reason, exsitu surface analysis was implemented in this work to characterize the treated surfaces. Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS) and Field Emission Auger Electron Spectroscopy (FE-AES) were used for that purpose.



Figure 1.3: Schematic representation of the research approach implemented in this study.

In the first part of this work (Chapter 2), the formation of the Zr-based conversion coatings on different metals are studied and compared using in-situ electrochemical analysis and ex-situ surface analytical techniques. The formation of the films are studied in-situ by recording the OCP

during the immersion of the metals in the conversion bath. The surface composition and thickness of the resulting conversion layers were examined by means of XPS, AES depth profiling and FE-AES. This is followed, in Chapter 3, by an investigation of the effect of convection on the deposition of Zr-based conversion coatings on different metals. In this section, different stirring rates are applied in the conversion bath to assess the influence of this variable on the chemistry, thickness and kinetics of formation. The observed trend is analyzed considering the effect of the convection on the different stages involved in the mechanism of formation of conversion films. In Chapter 4, the influence of the surface hydroxyls on the deposition of the Zr-based conversion coatings on AA6014 is studied. For that purpose, different model surface conditioning treatments were applied in order to form oxide films with different hydroxyl fractions and similar oxide layer thicknesses before the formation of the Zr-based conversion coatings. The in-depth elemental distribution, thickness and surface chemistry of the samples before and after the deposition of the conversion coatings were evaluated ex-situ by means of AES depth profiles and XPS. The observed behavior as a function of the initial hydroxyl fraction was correlated to the initial stage in the formation of the Zr-based conversion coatings. In Chapter 5, the local composition of Zrbased conversion layers formed on differently treated aluminium alloys was studied. Taking into account that the surface conditioning treatments modify the local composition of aluminium alloys, FE-AES was used to analyze these local and superficial elemental variations before and after the deposition of the Zr-based conversion layers. Surface maps, localized spectra and depth profiles were acquired for that purpose. In the last chapter, Chapter 6, a comparison of the effect of the surface hydroxyls on the deposition of Zr-based conversion coatings on different metals is presented. In this chapter, the same approach to the one implemented in Chapter 4 was applied for cold rolled steel specimens. These results are compared extensively with the ones presented in Chapter 4 for AA6014 and the ones reported by Taheri et. [14] in a similar study made for pure zinc substrates.

1.5. References

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Chapter 2

Initiation and growth of Zr-based conversion coatings on multimetal surface

In this Chapter, a surface pre-treatment based on a modified Zr-based conversion solution with addition of copper was studied as a replacement of the phosphating process. The main purpose of this study is to compare the formation mechanism and kinetics of Zr-based conversion coatings on three different base substrates: Aluminium alloy (AA) 6014, cold rolled steel and hot dip galvanized steel. For that purpose, Open Circuit Potential (OCP) measurements during the deposition of the conversion coatings are performed in combination with different ex-situ surface characterization techniques. The elemental distribution was analyzed by means of (Field Emission) Auger Electron Spectroscopy (FE-AES) depth profiles and mappings. Furthermore, the surface chemistry of the conversion layer was evaluated by X-Ray Photoelectron Spectroscopy (XPS). The results showed that while the mechanism of formation is similar for the different substrates, the rate of formation strongly depends on the substrate type. Additionally, the thickness and lateral and in-depth elemental distribution of the Zr-based conversion layers also largely depend on the underlying metal.

Keywords: Zr-based conversion coatings, Open Circuit Potential, FE-AES maps, depth profiles, XPS.

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2.1. Introduction

Surface pre-treatments are used on metal surfaces before application of organic paints. The purpose of this process is to promote better adhesion of organic paints and improve the corrosion protection of the underlying metal. One of the most effective pre-treatments is the application of chemical conversion coatings, which are formed by combined anodic dissolution and deposition processes on the metal substrate during immersion in the pre-treatment solution. Chromate-containing conversion coatings have been used for many years for this purpose. However, over the last decades, chromate pre-treatments are recognized to represent an environmental and health hazard in their use and disposal. For this reason, the use of this type of conversion coatings have been used as surface pre-treatment in a wide variety of industrial applications, such as the automotive and appliance industries. However, phosphate conversion coatings are being replaced because of several drawbacks from environmental, energy and process points of view [3, 4].

Among the chromate-free and environmentally friendly pre-treatments developed so far, the application of Zr-based conversion coatings by immersion in a hexafluorozirconic acid has gained acceptance [5-8]. They are currently introduced in several industrial applications, such as in the automotive industry. In order to beat the performance standards of the phosphating systems, it is nevertheless necessary to have a better understanding of the deposition mechanism of alternative conversion coatings. Despite the fact that several studies have been performed recently, most of them were focused on single base substrates, for example aluminium alloys. Such studies have shown that deposition of Zr/Ti conversion layers starts in the vicinity of the cathodic particles present at the aluminium alloy surface [9-10]. Andreatta et al. combined open circuit potential measurements with scanning electron microcopy and scanning Kelvin probe force microscopy to describe the formation mechanism of Zr/Ti conversion coatings on AA 6061 [11]. Laha et al. [12] used spectroscopic ellipsometry to measure the thickness of Zr/Ti coatings on AA 1050. Puomi et al. [13] showed that the Zr-based conversion coatings on hot dip galvanized steel and Galfan steel is mainly composed of ZrO₂ and their thickness is less than 50 nm. Verdier et al [14, 15] studied the effect of the fluoride concentration and pH in the deposition of Zr/Ti conversion coatings on

AM60 magnesium alloy. It was found that the film formation is facilitated when the pH is increased and inhibited when the fluoride concentration is increased. Adhikari et al. [16] proved that the addition of copper in the hexafluorozirconic acid solution accelerates the deposition of Zr-based conversion coatings on pure aluminium, iron and zinc.

Nowadays the automotive industry is focused on the design of cars with higher strength and lower weight. As a consequence most new cars structures contain a combination of different metals. Taking this into consideration, the formation mechanism and kinetics of Zr-based conversion coatings are studied in this work on three different base metal substrates. A copper modified hexafluorozirconic solution is applied, which is similar to the one used by Adhikari et al [16]. To that purpose, a similar approach as proposed by Campestrini et al. was followed to study the formation of chromate conversion layers on aluminium alloys [17]. Open Circuit Potential (OCP) measurements were used in combination with X-ray Photoelectron Spectroscopy (XPS), (Field Emission) Auger Electron Spectroscopy (FE-AES) depth profiles and mappings to investigate the growth of Zr-based conversion coatings on AA6014, cold rolled steel and hot dip galvanized steel.

2.2. Experimental

2.2.1. Materials and sample preparation

In this work, unpolished samples of AA 6014 (Mg \leq 0.8 wt%, Fe \leq 0.35 wt%, Si \leq 0.6 wt%, Cu \leq 0.2 wt%, Mn \leq 0.2 wt%, balance Al), hot dip galvanized (5-20 mg/m² Al, balance Zn) steel and cold rolled steel (C \leq 0.1 wt%, Mn \leq 0.50 wt%, P \leq 0.030 wt%, S \leq 0.035 wt%, balance Fe) supplied by Henkel AG & Co. KGaA (Düsseldorf, Germany) were used. All the samples were ultrasonically cleaned in ethanol for five minutes and dried with air. Then the samples were alkaline cleaned for 3 minutes in a 3 vol.% potassium hydroxide solution at 57 °C and magnetically stirred at 150 rpm. The pH of this solution was adjusted to 10.8 at 57 °C with phosphoric acid at 10 vol.%. Once the samples were alkaline cleaned, they were rinsed with deionized water and dried with air. For the ex-situ surface characterization, Zr-based layers were deposited by dipping the sample for 90 s in

a modified hexafluorozirconic acid solution (Zr < 200 mg/l) with 30-50 ppm of non-hazardous components of Cu provided by Henkel AG & Co. KGaA. The pH of this solution was adjusted to 4.0 with ammonium bicarbonate at 15 vol.%. Finally the samples were rinsed in deionized water and dried with air.

2.2.2. Experimental approach

Open Circuit Potential measurements (OCP) were performed during dipping in the modified hexafluorozirconic acid solution for 200 s, in order to study the electrochemical response of the different base substrates during the deposition of the coatings in-situ and as a function of time. For that purpose, a Solartron SI 1287 potentiostat and Saturated Calomel reference Electrode (SCE) were used. It was found that for all base substrates, except for the first 3 seconds, the deviation obtained in repeated three different measurements was in the order of 7 mV. As a result, the OCP measurements shown in this manuscript can be considered typical and reproducible.

Elemental depth profiles were obtained using a PHI 650(SAM) with a LaB₆ cathode and a Cylindrical Mirror Analyzer (CMA). The base pressure in the analysis chamber was $3x10^{-10}$ Torr. A primary electron beam with an energy of 5 keV and an emission current of 1 μ A incident on the sample surface at 30° to the normal. Ion sputtering was performed with a PHI 04-303 ion gun and 5 keV Ar ions (emission current of 20 mA and Ar pressure of 10 mPa). The ion beam was used at intervals of 1 minute and impinged on the sample surface at 50° to the normal. The recorded spectra were analyzed with the Multipak V8.0 software.

Applying a JEOL JAMP9500F FE-AES spectrometer, high-resolution mappings of the Zr-based conversion coatings were obtained. Using a magnification between 10000x and 20000x, maps of zirconium, copper, and the metal substrate were obtained employing an electron beam of 10 keV and 25 nA at an angle of incidence of 60°. The data was extracted and processed using the JEOL Image Investigator V1.04 software.

To study the surface chemistry of the samples, X-ray Photoelectron Spectroscopy (XPS) analysis was performed with a PHI 1600/3057 instrument using an incident X-ray radiation (Mg $K_{\alpha 1,2}$ = 1253.6 eV). All the measurements were done at an angle of 45° with respect to the sample surface. The spectra obtained on the conversion coatings were shifted to set the C-C/C-H components of the C 1s peak at a binding energy of 284.8 eV to correct the sample charging [18]. The evaluation of the Zr 3d_{3/2}, Zr 3d_{5/2}, Al 2p_{3/2}, Zn 2p_{3/2}and Fe 2p_{3/2} peaks was carried out using the PHI Multipak V8.0 software. The curve fitting was done after removal of a Shirley-type of background. A constrained fitting procedure was used in which the mixed Gauss-Lorentz shapes for the different fit components in the peaks were allowed to change in the 80-100 % region.

2.3. Results and discussion

2.3.1. Open circuit potential during the deposition

The evolution of the OCP in the conversion bath is shown in Figure 2.1 for AA 6014, cold rolled steel and hot dip galvanized steel. In the case of the AA 6014 the potential initially decreases from -0.35 V_{SCE} towards a minimum at -0.76 V_{SCE} after 50 s. Then it increases again until a stable potential is reached at -0.55 V_{SCE}. For the hot dip galvanized steel, the potential drops from -0.93 V_{SCE} to -0.94 V in 10 s, and then increases until a stable potential is achieved at -0.91 V_{SCE}. For the cold rolled steel the potential drops rapidly from -0.35 V_{SCE}, and instead of approaching a minimum, the potential declines less drastically until a relatively stable potential is reached at -0.58 V_{SCE}.

The initial decrease in the potential for the three substrates can be attributed to the activation of the metal surface due to the interaction with the free fluorides present in the conversion bath. The activation mechanism includes the replacement of the outer part of the metal oxides by metal fluorides, which are easier to dissolve than the original metal oxides [19]. The overall chemical dissolution process of metal oxides in contact with free fluorides has been proposed by Žutić et al [20]. Throughout this process, the metal oxides are thinned enabling electron tunneling and metal ion migration [21]. A change in the charge distribution and an increase in both the ionic and

electronic conductivity of the oxide film are expected, enhancing the electrochemical reactions such as the anodic dissolution of the metal [22]. The ionic conductivity is increased mainly because of the formation of vacancies, which cause an increase of the transport of metal ions through the oxides layer [23]. The fact that this drop occurs at different potentials depends largely on variations of ionic and electronic conductivities of metal oxides with the type of substrate. The chemical dissolution is surely affected by the surface chemistry of the metal oxides [24-25] and also the thickness of the oxides layers will play a role [17]. However, AES depth profiles recorded prior to the deposition of the coatings on the samples indicated that the oxide layer thickness for all the substrate materials is around 5 nm.



Figure 2.1: OCP evolution during the deposition of the Zr-based coatings

Although it is yet unknown whether a complete dissolution of the oxide layer is required to start the deposition of the Zr-based film, it is nevertheless accepted that the deposition of Zr is triggered by a local increase of the pH at the metal/solution interface by the hydrogen evolution and oxygen reduction reactions [9, 14, 26]. In the case of the AA 6014, the cathodic surface intermetallics can be responsible for this local increase in the pH, but for the cold rolled steel and hot dip galvanized steel it may be necessary to accelerate the conversion layer formation by the generation of additional cathodic sites on the substrate surface. Taking this into consideration, copper is added to the conversion bath. If Cu^{2+} ions are present in the solution the deposition of Cu occurs on the metal surface, changing the hydrogen evolution and oxygen reduction reaction at those sites [2730]. As an anodic counter reaction to the formation of elemental Cu at the surface, dissolution of the substrate material takes place.

The presence of a minimum in OCP of the AA 6014 and hot dip galvanized steel is because a higher cathodic activity is promoted by the Cu deposition, hydrogen evolution and oxygen reduction reactions. The absence of an OCP minimum for the cold rolled steel indicates that an anodic activity is predominant during the formation of the conversion film. Despite the potential decrease throughout the whole process, the deposition of Zr-based layer on cold rolled steel occurs during this decay [31]. The presence of a plateau region in the later stages of the OCP measurement indicates that a dynamic equilibrium between the anodic and cathodic reactions is reached. This suggests a lateral surface coverage of the conversion coating. In this part of the process, further deposition is expected that leads to an increase of the layer thickness without changes in the potential [11].

2.3.2. Surface characterization

In order to characterize the formation of the Zr-based conversion layer on the different metals, XPS as well as FE-AES depth profiles and mapping were used to compare the elemental distribution and surface chemistry of the resulting coatings. Auger depth profiles were recorded to study the elemental composition and thickness of the conversion layers on the different substrates. Three examples of Auger depth profiles acquired on the Zr-based conversion coatings of the three different substrates are shown Figure 2.2 a), b) and c) for AA 6014, cold rolled steel and galvanized steel respectively. A relatively large carbon content at the surface that decays with sputtering time is observed. This large superficial carbon content can be attributed to carbon-based contaminations at the surface of each sample. The two major elements at the top part of the conversion coatings increases in the initial part of the depth profile and then drops gradually. The increase of the Zr concentration together with the O amount in the film suggests that Zr is mainly present in the form of oxide/hydroxide. The concentration of the base metal element is low at the surface of the film and

gradually rises. However, the percentage of the base metal increases in zones where Zr is still present. From this observation the presence of an interphase composed by Zr and base metal oxides/hydroxides could be inferred. This behavior could also be attributed to the roughness of the samples. Moreover, a broadening of the interphase due to the ion sputtering is expected.

Following the model proposed by Campestrini et al [17], the thicknesses of the top and total layer (top part plus interphase) of the conversion coatings were calculated and are presented in Figure 2.2 d). According to this model, the top layer thickness is defined as the distance necessary to decrease the Zr peak-to-peak intensity line to 50% of its maximum value. Meanwhile, the total layer thickness is the distance in which the intensity of the base metal line reaches 50% of its maximum value. As observed in Figure 2.2 d) the thickest top layers were obtained for the hot dip galvanized steel, followed by cold rolled steel and AA 6014, respectively. This indicates that the kinetics of deposition largely depend on the base metal. On the other hand, combining the concept of top and total layer with the results showed in Figure 2.2 d), it can be noticed that the hot dip galvanized steel had the thickest coating/metal interphase, followed by AA 6014 and cold rolled steel, respectively. The deviations in the top and total layer of the conversion coatings may be attributed to the roughness of the coatings.





Figure 2.2: AES depth profiles of Zr-based conversion coatings on a) AA 6014, b) cold rolled steel and c) hot dip galvanized steel. d) Top and total layer thickness measured for the conversion layers.

Even though Cu and F were detected in all the samples, the content of these elements was low compared to the Zr, O and the base metal. Figure 2.3 a) and b) show the same depth profiles presented in Figure 2.2, but only illustrate the results obtained for Cu and F, respectively. The amount detected in all the measurements is higher than the detection limit of the equipment (about 1 at%). The fact that the amount of F within the film is low compared to the oxygen suggests that Zr is mainly present as an oxide rather than fluoride. In both depth profiles it is evident that the Cu and F concentration decreases mildly throughout the thickness of the coating. The reason of this behavior is that a part of the formed compounds of these elements may remain in the conversion layer during the deposition process. Nevertheless, the fact that Cu and F are found underneath the film indicates that these elements act as initiating elements for the deposition of the Zr-based conversion coating.





Figure 2.3: a) Cu and b) F AES depth profiles of Zr-based conversion layers on different substrates

Figure 2.4 shows the FE-AES Cu maps for the conversion coatings deposited on the three different metals. A more inhomogeneous distribution of Cu is present on the AA 6014, and islands from 0.2 to 2 µm in diameter with a higher concentration of Cu are observed. Hot dip galvanized steel surfaces indeed exhibit an increased lateral inhomogeneity. However, the differences between areas of low and high Cu concentration on AA 6014 are by far higher than on cold rolled steel or hot dip galvanized steel. This lateral Cu distribution can be attributed to the mechanism and kinetics of surface deposition of Cu. In order to start the Cu deposition, it is necessary to dissolve the metal oxides [27, 30]. A lateral local variation of oxide film thickness may influence local oxide thinning kinetics. Therefore, the dissolution of the oxides is finished first at locations of thin oxide films, allowing more time for the Cu displacement reaction to take place [32]. On the other hand, it is important to mention that Zr and base metal FE-AES maps, not shown here, proved that these elements were evenly distributed on all the substrates.





Figure 2.4: FE-AES Cu maps of Zr-based conversion coatings on a) AA 6014, b) cold rolled steel and c) hot dip galvanized steel.

Figure 2.5 a) shows the XPS spectra for the Zr-based conversion coatings on each metal substrate. All the elements identified with AES were also seen by means of XPS. Although the Cu 2p and Cu LMM peaks were observed in the XPS survey, their signal was too weak to be analyzed. Figure 2.5 b) shows an example of the Zr 3d peak. After fitting, the peak can be divided in two peaks; Zr $3d_{5/2}$ and Zr $3d_{3/2}$. As indicated in Figure 5 b), these peaks are located at a binding energy of 182.5 and 184.9 eV, respectively. According to the literature, these peaks correspond to ZrO_2 [33, 34]. The absence of extra peaks shows that if ZrF_4 is present, it can only be in small amounts.





Figure 2.5:XPS a) survey and b) Zr 3d spectra of the conversion layer on cold rolled steel.

Figure 2.6 shows the XPS spectra of the metals in the Zr-based conversion coatings deposited on the different substrates. For the AA 6014, the three compounds found after the fitting of the Al 2p spectra (see Figure 6 a)) were Al₂O₃, Al(OH)₃ and AlF₃[35, 36]. For the cold rolled steel (see Figure 6 b)) iron oxide, FeOOH and FeF₃ [37, 38] were found. And finally, for hot dip galvanized steel (see Figure 6 c)) ZnO and ZnF₂ [39, 40] are observed. The presence of these metallic fluorides is also in accordance with the thermodynamic calculation of these metals in F⁻ containing solutions presented by Xue et al [41]. Moreover, it confirms the mechanism of metal oxide dissolution in this system. The fact that metal oxides/hydroxides were detected may suggest that the complete dissolution of metal oxides due to its interaction with the free fluorides does not occur.





Figure 2.6: XPS a) Al, b) Fe and c) Zn $2p_{3/2}$ spectra in the conversion coating on the respective substrates.

Figure 2.7 summarizes the formation of the Zr-based conversion films of three different metal surfaces. The resulting Zr-based conversion layers are mainly present in the form ZrO_2 . FE-AES depth profiles have shown the presence of an interphase composed by a mixture of Zr and metallic oxyhydroxides. It was found that the resulting conversion layer and interphase are thicker on hot dip galvanized steel. Regions with higher concentration of Cu were found for the conversion coatings deposited on AA 6014.



Figure 2.7: Schematic drawing of Zr-based conversion layers on different substrates.

2.4. Conclusions

This work was focused on the formation process and characterization of modified Zr-based conversion coatings on three different metals. This process is initiated by the oxide/hydroxide layer dissolution, which is accompanied the by anodic dissolution reaction of each metal. The kinetics of this step occurred to be dependent on the surface chemistry of the metal oxide. Subsequently, the deposition of the conversion layer starts due to an increase of the pH promoted by the hydrogen evolution and oxygen reduction reactions. This pH increase is supported by the preceding deposition of Cu. Using AES depth profiles, small amounts of Cu and F were identified throughout the coatings, validating the role of these elements in the formation mechanism. FE-AES Cu maps for conversion coatings deposited on cold rolled steel and hot dip galvanized steel showed that the Cu was evenly distributed over the surface. For the AA 6014 islands with higher concentration of Cu were observed. This behavior indicates that the deposition of Cu is affected by the local metal oxide/hydroxide dissolution and metal substrate. AES depth profiles show that the hot dip galvanized steel had the thickest conversion films, followed by cold rolled steel and AA 6014, respectively. This suggests that the kinetics of the deposition process depends on the substrate. XPS measurements have shown that most of the Zr is present in the form of ZrO_2 . Additionally, depending on the substrate compounds such as Al₂O₃, ZnO, FeOOH, FeF₃, ZnF₂ and AlF₃ were found in the coatings in smaller amounts as compared to the ZrO₂.

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Chapter 3

The effect of convection on the formation of Zr-based conversion coatings on multi-metal surfaces

The present study investigates the effect of different conversion bath agitation and stirring conditions on the generation of Zr-based thin film conversion coatings for steel, zinc galvanized steel and aluminium substrates. Therefore, samples were immersed in a copper containing hexafluorozirconic acid solution. Film formation was monitored in-situ via Open Circuit Potential (OCP) measurements recorded during the pre-treatment of the samples in solution. The resulting thickness and elemental distribution of the obtained Zr-based coatings formed with and without stirring were analyzed ex-situ by means of high-resolution Auger Electron Spectroscopy (AES) depth profiles. Under the studied conditions, the conversion film thickness on AA6014 and cold rolled steel increased three and two times as a result of stirring. For hot dip galvanized steel, a thickness increase of 400 % was achieved. The data point at mass transfer as the dominant factor for film formation. In this context, specific relations for each metal substrate type were detected.

Keywords: Zr-based conversion coatings, convection, OCP, AES depth profiles.

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3.1. Introduction

The application of ultra-thin conversion films on metallic substrates is commonly used to improve the corrosion resistance of the metal surface and also the adhesion performance of subsequently applied organic coatings [1-6]. Currently, this technology is about to replace conventional phosphating in the automotive industry due to several advantages including lower costs as well as facilitated process control and waste water treatment [7-14].

In this process, conversion films are often obtained after immersion in a hexafluorozirconic or hexafluorotitanic acid solution. During the first seconds, free fluorides present in the solution dissolve the oxide layer of the substrate [15-21]. Thereby, anodic dissolution of the metal starts or gets strongly accelerated. Oxygen reduction and hydrogen evolution as counter reactions then induce an increase of the pH at the metal/solution interface [16-21]. If hexafluorozirconic acids are applied as one of the active components of the conversion bath composition, F⁻ ligands of the zirconium-fluoride complexes are exchanged at this stage by hydroxide ligands. As a result, Zr-hydroxide species with low solubility precipitate on the substrate surface and dehydration processes subsequently initiate the generation of Zr-oxide films. Layer growth kinetics and mechanisms can be influenced by the presence of species with high precipitation tendency in the conversion bath [22-23]. For example, copper ions quickly deposit on the substrates, get reduced and form copper and copper oxide agglomerates, which act as additional sites for the local alkalization required to support the generation of the conversion film [22-25].

Several authors already studied the aspects of film formation in stagnant hexafluorozirconic acid solutions on various substrates including magnesium, cold rolled steel and hot dip galvanized steel [19, 27-28]. However, the convection of the conversion coating bath is known to significantly impact the layer formation kinetics, as well. Mechanistic analysis of concentration effects at the metal/solution interface under mass- and diffusion-control typically occurs on a microscopic scale, e.g. with rotating disc electrodes. Nevertheless, the translation of such results to the characteristics of the pre-treatment process in macroscopic dimensions, e.g. in automotive body lines, is not easy. Especially the role of functional additives like copper as a function of different bath agitation conditions is not understood in detail yet, too.

Therefore, the present study follows the approach of simulating conversion coating formation on a semi-macroscopic scale of one liter bath solution on sample surface areas of some cm². Film growth is tracked via Open Circuit Potential (OCP) measurements under different bath convection and agitation conditions. The obtained layer compositions are investigated with Auger Electron Spectroscopy (AES) depth profiles of high surface sensitivity to better understand the effect of the copper presence and its local distributions in the films. The results will support cross-correlations to previous studies about copper containing Zr-based conversion treatments on different metals [24]. They will also support knowledge transfer between the analysis of microscopic aspects of film formation to the process characteristics in 'full'-macroscopic scales that are especially relevant for industrial bath dimensions.

3.2. Experimental

3.2.1. Materials and sample preparation

Unpolished specimens of AA6014 (Mg \leq 0.8 wt.%, Fe \leq 0.35wt.%, Si \leq 0.6wt.%, Cu \leq 0.2wt.%, Mn \leq 0.2wt.%, balance Al), hot dip galvanized (5–20 mg/m² Al, balance Zn) steel and cold rolled steel (C \leq 0.1wt.%, Mn \leq 0.50wt.%, P \leq 0.030wt.%, S \leq 0.035wt.%, balance Fe) provided by Henkel AG & Co. KGaA were used. They were ultrasonically cleaned in ethanol for 5 min and dried with compressed air. Subsequently, an alkaline cleaning step was performed by immersing the samples for 3 min in a 3 vol.% potassium hydroxide solution at 57 °C and a pH of 10.8, adjusted by 10 vol.% phosphoric acid. The Zr-based conversion coatings were applied by immersing the specimens in a PVC beaker (diameter = 8 cm) containing 1 l of a hexafluorozirconic acid solution (room temperature, zirconium \leq 200 mg/l, pH = 4, adjusted by 15 vol.% ammonium bicarbonate solution) with small amounts of non-hazardous components of copper [20, 22] supplied by Henkel AG & Co. KGaA.

For ex-situ AES surface analysis measurements, sample sheets were introduced into a specimen holder (circular in shape, with a total diameter of 3.2 cm). Due to a cover fixation ring, the sample surface was positioned recessed by about 8 mm with respect to the front of the specimen holder.

Thereby, indirect approach flow conditions for the pre-treatment of inside surfaces of car body shells were simulated. Effectively, a circular sample surface area of 2.8 cm² was exposed to the conversion bath. Immersion occurred during 90 s while the solution was either stagnant or magnetically stirred at 400 rpm (length of stirring bar = 4 cm, diameter = 8 mm). The sample was positioned in parallel to the flow at a distance of 5 cm to the bottom of the beaker and outside of any turbulent stirring vortex to ensure laminar convection conditions at its surface. Afterwards, all samples were rinsed in deionized water and dried with compressed air.

3.2. Experimental approach

Using a Solartron SI 1287 potentiostat and a Saturated Calomel reference Electrode (SCE), the Open Circuit Potential (OCP) of the investigated samples were recording during the initial 300s while immersed in the conversion bath solution. Again 3.14 cm² of the sample surface were exposed to the solution using the specimen holder mentioned above. The treatment was exactly equivalent to the procedure described in chapter 2.1, especially regarding the positioning of the sample. The only difference refers to varying stirring rates, which range between no stirring (0 rpm), 200 rpm, 400 rpm, 600 rpm and 800 rpm. Electrically contacted from the back, the potential was recorded every 1 s and given vs. the SCE electrode scale. The OCP transients were reproduced at least three times to ensure good reproducibility with standard deviation of about 7 mV.

AES depth profiles were acquired using a PHI 650 spectrometer with a cylindrical mirror analyzer. Measurements were performed at a pressure of the analysis chamber of around around 3×10^{-10} torr, a primary electron beam of 5 kV and an emission current of 1 μ A and at an incident angle of 30° with respect to the surface normal of the sample. Argon sputtering was applied using Ar⁺ ions with energy of 5 keV, an emission current of 20 mA and a Ar⁺ pressure of 10 mPa. The results were processed using the PHI Multipak V8.0 software. Thickness values are given as a function of the sputter time instead of a depth scale due to the dependency of the sputter rate on the chemical composition and morphology of the matrix. However, a value of 12 nm/min may be nevertheless used to roughly estimate the investigated film thicknesses.

3. Results and discussions

3.1. Open Circuit Potential during the deposition of the Zr-based conversion films

Figure 3.1 shows potential transients recorded during immersion of AA6014 samples in the conversion bath at different stirring rates. Similar curves are observed for all convection conditions. Initially, the potential drops to a local minimum after 35 to 50 s depending on the stirring rate and then rapidly increases for the next 40 to 60 s. Afterwards, it slowly increases for the remaining time of the experiment. For the aluminium alloy, the initial potential decay during the first seconds of immersion indicates dominant anodic processes due to the dissolution of the oxide film by free fluorides [29]. At the minimum potential cathodic reactions, in particular hydrogen evolution, oxygen reduction and copper deposition [24] get that accelerated due to thinning of the aluminium oxide that they dominate the overall current densities [30]. A subsequent drastic increase in the potential refers to conversion coating formation on the aluminium surface. As soon as this increase flattens out and converges towards a plateau, full coverage of the aluminium surface by the Zr-based conversion film is achieved. Longer immersion times then primarily promote an increase of the film thickness [20]. The OCP response of cold rolled steel during immersion in the conversion coating bath at different stirring rates is presented in Figure 3.2. For all specimens, the potential initially rapidly drops during the initial 25 s. Afterwards, it slowly, but still continuously decreases during the following 75-100 s, except for the sample immersed in stagnant solution, which showed a potential decline until the end of the experiment. For the specimens immersed in solution stirred at 600 rpm and higher, a slight increase in the potential is observed after 100-150 s. It is distinctly less pronounced than for the aluminium samples, because the kinetics of anodic dissolution reactions on cold rolled steel in a conversion bath solution of pH 4 proceed much more accelerated during the Zr-deposition process [24]. Figure 3.3 shows the OCP evolution of hot dip galvanized steel in the conversion bath at different stirring rates. Unlike AA6014, the potential quickly drops to a minimum in less than 10 s for all investigated stirring conditions (only visible for low stirring rates of 0-200 rpms in Figure 3), then rapidly increases again and converges towards a stable plateau. This constant potential is achieved in less than 75 s for all tested stirring rates.



Figure 3.1: OCP responses of AA6014 in the conversion bath solution at different stirring rates.



Figure 3.2: OCP evolution of cold rolled steel in the conversion solution at different stirring rates.



Figure 3.3: OCP evolution of hot dip galvanized steel in the conversion solution at different stirring rates.

Considering that the regular immersion time in the Zr-based conversion coatings is in the order of 90 s, a suitable indicator to compare the effect of stirring on the formation of the films is the potential after this immersion period. Figure 3.4 displays the OCP at 90 s of immersion of the three different metals as a function of bath convection. For AA6014, a potential of -0.68 V_{SCE} was detected after 90 s. More anodic values of approximately 0.25 V_{SCE} were determined for stirring rates of 200 rpm and higher (see Figure 3.4a). For cold rolled steel Figure 3.4 b) indicates a linear correlation between bath convection and potential increase. The OCP varies between -0.55 V_{SCE} and -0.45 V_{SCE} for stagnant and strongly stirred solution and almost evenly rises. Figure 3.4 c) shows the respective graph for hot dip galvanized steel. Its shape exhibits intermediate characteristics compared to those for steel and aluminium: A distinct potential increase between 0 and 200 rpm, a constant plateau between 200 and 600 rpm and a more pronounced final increase for 800 rpm. However, the overall potential changes between 0 and 800 rpm are low and only refer to 90 mV, which is distinctly less compared to aluminium (300 mV, see above) and slightly less than for cold rolled steel (about 100 mV). These results underline the strong dependency of the conversion coating formation kinetics on the substrate material as a function of the (indirect) liquid flow near the sample surfaces. Largest differences were observed between stagnant and slightly stirred conversion baths, whereas increased flow rates of > 200 rpm seem to have a relatively low impact on the shape of the OCP-graphs (see Figures 3.1 to 3.3), but nevertheless a detectable influence on the potential after 90 s of immersion (see Figure 3.4). Based on the obtained data optimized conversion layer characteristics may be expected at average bath convection, which refers to stirring rates of about 400 rpm.



Figure 3.4: Potential after 90 s of immersion in the conversion bath as a function of the stirring rate for a) AA6014, b) cold rolled steel and c) hot dip galvanized steel.
3.2. Ex-situ surface analysis of the Zr-based conversion coatings

AES depth profiles were acquired to study the effect of stirring on the elemental distribution and resulting thickness of the Zr-based conversion coatings. Figure 3.5 shows profiles recorded for the Zr-based conversion films deposited on the three different metals after 90 s of immersion in the stagnant conversion solution. Figure 3.6 presents the AES depth profiles of Zr-based layers formed after 90 s in the conversion bath stirred at 400 rpms. For all substrates and deposition conditions, a large content of carbon is detected during the first minute of sputtering as result of the exposure of the samples to the environment. Besides that, zirconium and oxygen are the predominant elements in the films at this stage. Previous results confirmed that the zirconium is present in the form of zirconium dioxide [12, 24]. Depending on the substrate, only small amounts of aluminium, iron and zinc are detected near the coating surface regardless of the stirring rate. These elements are mainly present in the form of metallic oxides, hydroxides and fluorides [24]. For all substrates and stirring rates, the zirconium and oxygen concentrations slowly decrease with the sputtering time and in any case, extended durations were required to reduce the zirconium content in films formed at 400 rpm compared to 0 rpm. This indicates increased coating layer thicknesses for film formation in stirred conversion bath solution. Thicknesses were determined according to the assumption that they refer to the time required to reduce the zirconium peak intensity by 50% [31]. Figure 3.7 shows the obtained results. The effect of layer thickness increase as a result of stirring of the conversion bath is most pronounced on hot dip galvanized steel, where the film thickness rises by a factor of four. For the AA6014 and cold rolled steel the thickness of the conversion coating is increased by three and two times in case of stirring with 400 rpms. These effects should be strongly dependent on the concentration gradients of all relevant species in the conversion solution near the substrate surfaces as well as by the correlated mass transfer reactions. At a pH of 4 and within a wide range of concentrations, the dissolution of aluminium oxides, for example, accelerates with increasing stirring rate due to higher concentrations of free fluorides at the substrate surface as the result of an accelerated mass transport [32]. This reduces the required time for oxide dissolution and increases the available time zirconium can deposit on activated and oxide-free sites of the aluminium matrix.



Figure 3.5: AES depth profiles of Zr-based conversion layers on a) AA6014, b) cold rolled steel and c) hot dip galvanized steel deposited in the conversion solution without stirring.



Figure 3.6: AES depth profiles of Zr-based conversion films on a) AA6014, b) cold rolled steel and c) hot dip galvanized steel deposited in the conversion bath with a stirring rate of 400 rpm.



Figure 3.7: Top layer thicknesses of Zr-based conversion coatings deposited on different metals in conversion baths at 0 and 400 rpm.

Figure 3.8 displays the maximum copper concentration in the conversion films, derived from AES depth profiles for the different metals and stirring conditions. The detected copper amounts are relatively small, but nevertheless above the AES detection limit of 1 at% and therefore valid for interpretation. For all substrates, the copper content significantly increases for stirring of the conversion bath at 400 rpm. This indicates an enrichment of copper rich cathodic sites at the surface, which stimulates the anodic dissolution of the metal, hydrogen evolution and oxygen reduction reactions [17, 18, 20, 22, 23]. Consequently, it will promote the local alkalization at the substrate/solution interface and support the precipitation of zirconium oxide/hydroxide. Figure 8 indicates three times larger copper concentrations in the conversion films on hot dip galvanized steel, two times larger concentrations on cold rolled steel and only about 50 % more copper on aluminium if samples were immersed in conversion baths stirred at 400 rpm. This tendency is roughly in line with the observations made for the overall Zr-layer thickness before, but the copper increase rate occurs to be lower in particular for cold rolled steel and AA6014. This points at substrate-dependent mass-transfer processes, especially as the copper deposition tendency differs between zinc, aluminium and iron surfaces [33]. As an additive in fluoride-containing solutions, copper precipitation kinetics will be especially influenced by the metal dissolution kinetics, too [24]. In other words, it has to be expected that the faster the fluoride attack on the oxide layer of the substrate occurs to electrochemically activate its surface, the earlier copper will start to deposit

[33-40]. Additionally, the effect of the forced convective mass transfer on the deposition of copper is known to be different for every metal [33-35]. To analyse these effects more in detail, rotating disc electrode measurements for conversion baths with differing copper, free fluorides and zirconium amounts and convection conditions will be suited, but go beyond the scope of the present study. Anyhow, basic learnings refer to the fact that coating weight increases for zirconium and copper differ significantly even for conversion solutions with optimized bath convection. This allows for a specific control of the relative ratio of precipitated zirconium and copper species also for inner surfaces of pre-treated specimens that are subject to more indirect laminar flow conditions - a fact that is highly relevant for industrial application, in particular for the processing of inner surfaces of car body shells.



Figure 3.8: Maximum Cu concentration detected by means of AES depth profiles for the Zr-based coatings deposited on different metals in conversion solution at 0 and 400 rpm.

3.4. Conclusions

This work focused on studying the effect of bath convection on the formation mechanism and kinetics of Zr-based conversion coatings on AA6014, cold rolled steel and hot dip galvanized steel. Indirect laminar flow conditions simulated the pre-treatment of inside surfaces of car body shells on a semi-macroscopic scale, but also allow for comparison to previous results of fundamental

microscopic investigations of conversion films. The following conclusions can be drawn:

- Open circuit potential transients confirm optimized layer deposition at intermediate stirring of the pre-treatment solution at 400 rpm and for an immersion time of at least 90 s. Under these conditions almost steady-state kinetics of conversion film growth are achieved on steel, zinc and aluminium. Initially significant differences in the shape of the graphs, in particular decline of the potential due to anodic substrate dissolution processes, are balanced at that time and occur to be overcompensated by cathodic zirconium and copper deposition. Moreover, variations of the liquid flow near the substrate surface, stimulated by stirring between 200 and 800 rpm, seem to have a rather negligible impact on the potential transients.
- Convection of the pre-treatment solution generally accelerates all relevant mechanistic steps of conversion film formation. It has the strongest impact on aluminium (potential shift of ≈ 300 mV), but distinctly minor effects on the OCP transients of steel (≈ 100 mV) and zinc (≈ 90 mV).
- Compared to sample immersion in stagnant solution, the conversion film thickness increases by a factor of four on zinc, of three on steel and of two on aluminium surfaces as a result of forced convective mass transfer for a treatment time of 90 s and a stirring rate of 400 rpm. In general, smaller factors of three on zinc, two on steel and 0.5 on aluminium were determined for the increase of the copper content embedded in the pre-treatment layer under the same conditions. On the one hand, these results demonstrate the path to controlled relative ratios of precipitated zirconium and copper species by a specific adjustment of the conversion bath convection. On the other hand, they confirm substrate-dependent variations of film growth kinetics. A prediction of coating weights for different deposition conditions consequently requires careful elemental layer analysis and cannot solely rely on (online) monitoring of the open circuit potential.

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Chapter 4

The influence of surface hydroxyls on the formation of Zr-based conversion coatings on AA6014 aluminium alloy

This study investigates the influence of surface conditioning on the deposition of Zr-based conversion films on AA6014. For that purpose, different treatments were used to control the formation of well-defined oxides layers with different hydroxyl fractions and similar thicknesses prior to the conversion layer formation process. The elemental distribution and surface chemistry of the treated samples before and after the formation of the Zr-based conversion layer were evaluated by Auger Electron Spectroscopy (AES) depth profiling and X-ray Photoelectron Spectroscopy (XPS). Moreover, the Open Circuit Potential (OCP) evolution as a function of time was recorded during the formation of the Zr-based conversion layers in order to evaluate the electrochemical surface activity and formation mechanism in-situ. The results have shown that a higher initial hydroxyl fraction encourages the formation of a thicker Zr-based layer.

Keywords: Zr-based conversion coatings, hydroxyl fraction, XPS, AES, Open Circuit Potential.

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4.1. Introduction

Conversion pre-treatments are applied on metal surfaces to improve the corrosion resistance and adhesion properties of a subsequent organic coating [1]. For many years, phosphate containing conversion pre-treatments have been used in the automotive industry for that purpose. However, this process has several drawbacks regarding the disposal of the conversion bath [2, 3]. Another disadvantage is the fact that most of the phosphating solutions operate above room temperature, which increases the overall cost of the process. Moreover, the phosphating process sometimes requires an extra sealing step to improve the overall performance of the coating. Consequently, new eco-friendly conversion pre-treatments are developed to replace the traditional phosphating systems. One of the most technically and environmentally accepted alternative is the Zr-based conversion coating. In this case, the converted layer forms while the metal substrate is exposed to a hexafluorozirconic acid solution [4-9].

The first stage in the formation of Zr-based coatings is the activation of the metal surface as a result of the interaction with free fluorides present in the conversion solution thinning and removing the original metal oxide [10, 11]. The reduction of the oxide layer thickness facilitates electron tunneling and metal ion migration as a result of an enhanced surface conductivity [12, 13]. So far, it is unclear whether the oxide layer is completely dissolved by the free fluorides before the deposition the Zr-based coating. Nevertheless, it is widely accepted that a local increase of the pH at the metal and solution interface initiates the film formation [14-17]. This increase in the pH can be accelerated if Cu species are added to the conversion bath, promoting the local deposition of Cu on the metal surface and consequently a local pH increase by stimulating the hydrogen ion and oxygen reduction reaction kinetics at these sites [18-20].

Surface conditioning alters the oxide chemistry of metal surfaces. It is well known that hydroxyl groups are present at the outer part of a metal oxide [21, 22]. For zinc surfaces, Taheri et al. [23] reported that the surface chemistry prior to the deposition of Zr-based coatings has a major effect on the formation of the Zr-based conversion coating and subsequently on the interfacial bonding properties between the metal and polymer phases. Following up on this prior research and

considering multi-metal applications in the automotive industry, this study is focused on understanding the effect of the hydroxyl fraction on the deposition of Zr-based films on differently treated AA6014 samples. To achieve that goal, ex-situ surface analytical techniques and Open Circuit Potential (OCP) measurements during the conversion pre-treatment have been combined to study the effect of the surface conditioning on the subsequent formation of the Zr-based conversion coatings. The initial surface hydroxyl fraction and elemental surface and in-depth distribution before and after the deposition of the Zr-based layer were assessed by means of X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) depth profiles.

4.2 Experimental approach

4.2.1. Materials and sample preparation

In this work, samples of AA6014 (Mg \leq 0.8 wt.%, Fe \leq 0.35 wt.%, Si \leq 0.6 wt.%, Cu \leq 0.2 wt.%, $Mn \le 0.2$ wt.%, balance Al) provided by Henkel AG & Co. KGaA were used. The samples were mechanically ground with SiC paper in subsequent steps and then polished to different grade diamond paste (9, 6, 3, 1, and 0.25 µm). All the specimens were degreased ultrasonically in ethanol for 5 minutes to obtain a reference sample surface state. In order to modify the hydroxyl fraction of aluminium oxides, different sets of the from now on called reference sample were exposed to one of the following treatments: acid, alkaline, pseudoboehmite and thermal. The acid treatment was performed immersing the samples for 30 s in a 30 vol.% nitric acid solution. Then, the specimens were rinsed in deionized water for 3 min and dried using compressed air. The so-called alkaline treated sample was obtained by immersing the substrate for 3 min in a 3 vol.% potassium hydroxide solution at 57 °C with stirring rate of 150 rpm. Using a phosphoric acid solution at 10 vol.%, the pH of this solution was adjusted to 10.8 at 57 °C. For the so-called pseudoboehmite treated samples, the substrate was immersed in boiling deionized water for 15 s. Then, the specimens were then allowed to dry for few minutes in an upright position. Finally, the thermally treated sample was prepared by heating the specimens in air for 24 h at a temperature of 275 °C. For the surface characterization of the Zr-based conversion coatings, a set of the differently treated specimens were immersed for 90 s in a modified hexafluorozirconic acid solution (Zr < 200 mg/l) with smaller amounts of non-hazardous components of Cu [18, 19] supplied by Henkel AG & Co. 41

KGaA with a stirring rate of 400 rpm. Using an ammonium bicarbonate solution at 15 vol.%, the pH of the solution was adjusted to 4.0.

4.2.2. Surface characterization

In order to characterize the surface chemistry of the treated samples before and after the deposition of the Zr-based conversion films, XPS analysis was conducted using a PHI-5600ci instrument with a monochromatic Al K α source. The pressure of the analysis chamber was kept at approximately 1×10^{-9} Torr. Narrow multiplex scans of the peaks were recorded using a pass energy of 23.5 eV, with a step size of 0.1 eV and a take-off angle of 45° with respect to the sample surface. Peak fitting was carried out using the PHI-Multipak software (Version 8.0) and conducting a Shirley background removal with a mixed Gauss-Lorentz shape. In order to correct the sample charging before starting the curve fitting, the spectra were shifted to set the C-C/C-H component of the C1s peak at a binding energy of 284.8 eV [24]. The χ^2 value of the peaks after fitting was lower than 1.5 for all of the measurements.

To evaluate the in-depth elemental distribution of the samples before and after the deposition of the Zr-based coatings, Auger Electron Spectroscopy (AES) measurements were performed using a PHI 650(SAM) equipped with a LaB6 cathode and a Cylindrical Mirror Analyzer (CMA). The pressure in the analysis chamber was approximately $3x10^{-10}$ Torr. An electron beam of 5 keV and 1 μ A at an angle of incidence of 30° with respect to the sample surface normal was applied. Argon sputtering with 5 kV Ar⁺, ion emission current of 20 mA and an argon gas pressure of 10 mPa was used. The data were processed using the PHI-Multipak software (Version 8.0). All the thicknesses were expressed as a function of the sputter time instead of depth in the films due to the dependence of the sputter rate on the matrix. The reproducibility of the AES depth profiles and XPS measurements was verified by triplication of the measurements.

4.2.3. Open circuit potential during the deposition of Zr-based layers

To study the electrochemical behavior of the differently treated samples during the conversion

coating formation in-situ and as a function of time, Open Circuit Potential (OCP) measurements were performed for 300 s in the Cu-containing hexafluorozirconic acid solution. These measurements were conducted using a Solartron SI 1287 potentiostat and Saturated Calomel reference Electrode (SCE). For all specimens, the deviation obtained within a threefold repetition of the measurements was in the order of 7 mV, except for the first 3 seconds. As a consequence, the OCP measurements presented are considered reproducible.

4.3. Results and discussion

4.3.1. Surface chemistry and elemental distribution of the treated samples

To study the surface chemistry of the treated samples, XPS measurements were performed. Figure 1 shows the XPS fitting of the C 1s and O 1s peaks of the alkaline treated sample. When the samples are exposed to the environment, different organic contaminants can absorb on the hydroxylated oxide surface [20]. As shown in Figure 4.1 a) the C 1s peak can be decomposed in C–C/C–H, C–COO_X, C–O, C=O and O–C=O/O–C–O[–] species [25-26]. The O 1s peak can be resolved in O^{2-} , OH[–] and the H₂O/COx sub peaks as shown in Figure 4.1 b).





Figure 4.1: XPS a) C 1s and b) O 1s peak fitting of the alkaline treated sample.

The hydroxyl fraction can be calculated from the O 1s peak fitting after subtracting the contribution of the surface contamination. Following the model introduced by McCafferty et al. [21], the resulting hydroxyl fractions of the different treatments were calculated. Figure 4.2 shows the average values obtained from this calculation. As observed in Figure 4.2, the lowest hydroxyl fraction of 13% is obtained for the thermally treated sample. The second lowest hydroxyl fraction of 22% is seen for the acid treated sample. For the reference, alkaline treated and pseudoboehmite treated samples, the hydroxyl fraction range is between 46 and 52%. The standard deviation in the results is around 2%. All these values, except the one for the alkaline treated sample, are in the same order of magnitude as those of reported by van den Brand et al. for the AA1050 [27].



Figure 4.2: Hydroxyl fraction for the differently treated samples.

To study the in-depth elemental distribution of the treated samples, AES depth profiles were recorded. Figure 4.3 shows the AES depth profiles for the acid, pseudoboehmite and thermally treated samples. The AES depth profiles for the alkaline treated and reference samples are shown in the Appendix. As observed in Figure 4.3 a) and b), the in-depth elemental differences between these two samples are very small. It is important to mention that for the thermally treated sample, as shown in Figure 4.3 c), Mg is detected within the oxide layer. This occurs due to the preferential oxidation during the thermal treatment, where the Mg is mainly present in the form of MgO [28]. Following the model proposed by De Laet et al. [29], the thicknesses of the oxide layer of the differently treated samples are calculated and presented in Figure 4.4. From these results, it can be concluded that the differences in the oxide layer thickness between the differently treated samples are very small.



Figure 4.3: AES depth profile for the a) acid, b) pseudoboehmite and c) thermally treated sample.



Figure 4.4:Oxide layer thickness for the differently treated samples.

4.3.2. Surface chemistry and elemental distribution of Zr-based films deposited on the differently treated samples

In order to characterize the formation of the Zr-based conversion coating, AES depth profiles and XPS measurements were performed to compare the elemental distribution and surface chemistry of the resulting coatings as a function of the different treatments. Two examples of the AES depth profiles for the Zr-based layers deposited on the pseudoboehmite and thermally treated samples are shown in Figure 4.5 a) and b) respectively. These profiles represent coatings deposited on samples with the highest and lowest hydroxyl fractions. The AES depth profiles for the Zr-based conversion coatings deposited on the acid, alkaline treated and reference samples are shown in the Appendix. For the pseudoboehmite treated sample, Zr and O are the predominant elements during the first minutes of sputtering. The concentration of Al is low in this part of the layer, indicating the formation of a well formed Zr-based conversion film. On the other hand, for the thermally treated sample, the amount of Zr detected during the first minutes of sputtering is considerably lower than that of the pseudoboehmite treated sample. The Al detected in this outer region is present in the form of aluminum oxide/hydroxide.



Figure 4.5: AES depth profiles of the Zr-based conversion layers formed on the a) pseudoboehmite treated sample and b) the thermally treated sample.

For all the specimens, the detected concentration of Cu and F is between 3 and 5 at%. Considering the low concentrations of these elements, it is difficult to directly elucidate the effect of the hydroxyl fraction on the presence of these two elements in the final Zr-based conversion coating. Furthermore, it can be noticed that the amount Al slowly increases as a function of the sputter time. These changes are observed in zones where Zr and O are also detected. As a result, it could be deduced that an interphase composed of a mixture of Zr and aluminium oxides exists. However, this behavior could also be related to the broadening of the interphase caused by the argon sputtering.

Using the model suggested by Campestrini et al. [30], the total layer thicknesses of the Zr-based

conversion films were calculated and are presented in Figure 4.6. The previously determined hydroxyl fraction before the application of the conversion films is also indicated. According to this model, the total layer thickness is defined as a depth in which the intensity of the aluminium peak reaches 50% of its maximum value. From the information given in Figure 4.6, it is evident that the total layer thickness of the thermally and acid treated sample is less than half the layer thickness on the alkaline, pseudoboehmite and reference samples. In order to have an approximation of the real thickness of the conversion layers formed on the differently treated samples, the depth of the crater after 1 min of argon sputtering was measured using Atomic Force Microscopy (AFM). From this measurement it was obtained that 1 min of argon sputtering removes around 10 nm of the conversion film. Taking this sputter rate into account (10 nm/min), the total layer thicknesses of the films can be estimated. They are equivalent to 6 nm for the acid and thermally treated sample and to 20 nm for the alkaline, reference and pseudoboehmite treated samples.



Figure 4.6: Total layer thickness measured for the Zr-based conversion layers deposited on the differently treated samples.

Figure 4.7 shows the maximum Zr concentration detected by means of AES depth profiles for the Zr-based layers deposited on the differently treated samples. The hydroxyl fraction of the treated samples before the deposition of the Zr- based conversion coating is also indicated. It can be noticed that the Zr content increases with the hydroxyl fraction. For the thermally and acid treated samples, which possess a hydroxyl fraction of 13% and 22% respectively, the maximum

concentration detected in the Zr-based film is below 8 at%. For the alkaline, reference and pseudoboehmite treated samples, which exhibit hydroxyl fractions between 46% and 52%, the Zr content is between 25 and 30 at%.



Figure 4.7: Maximum Zr concentration detected by means of AES depth profiles for the Zr-based films deposited on the differently treated samples.

Figure 4.8 a) shows the XPS spectrum for the Zr-based conversion layer formed on the alkaline treated sample. Note that all the elements detected by AES depth profiles were also identified by XPS. As shown in Figure 4.8 b), the Zr 3d peak can be divided in two sub-peaks; Zr $3d_{5/2}$ and Zr $3d_{3/2}$. These sub-peaks are located at binding energies of 182.5 and 185 eV, respectively, which correspond to ZrO₂ [31, 32]. In order to compare the relative amount of Zr deposited with respect to the Al as a function of the hydroxyl fraction, the areas of the fitted Zr 3d, Al 2p and Al 2s peaks were studied. To subtract experimental variations of the sample position versus the X-ray source and photoelectron detector, it is necessary to introduce the following normalization factors:



Figure 4.8: a) XPS spectrum and b) Zr 3d peak for Zr-based films deposited on the alkaline treated sample.

$$\Delta Zr = \frac{Zr3d \text{ area}}{Zr3d \text{ area} + Al2p \text{ area} + Al2s \text{ area}}$$
(1)

$$\Delta Al = \frac{Al 2p \text{ area} + Al2s \text{ area}}{Zr3d \text{ area} + Al2p \text{ area} + Al2s \text{ area}}$$
(2)

These normalization factors represent the relative amounts of Zr and Al detected on each sample. Figure 4.9 shows the average of these normalization factors obtained for the conversion layers deposited on differently treated samples. The hydroxyl fraction obtained before the application of the conversion layer for each treated sample is also indicated. As observed in Figure 4.9, the amount of Zr relative to Al detected by XPS increases with the hydroxyl fraction. Additionally, the amount of Al present on the surface of each treated sample increases when the hydroxyl fraction of the AA6014 is reduced. It should be noted that the normalization factors for Al and Zr shown in Figure 4.9 might be slightly affected by the overlapping of the Al 2s and Al 2p with the Cu 3s and Cu 3p peaks. This also applies to some of the XPS results reported in a previous publication [18]. An exact definition of the Cu-contribution to the Al-peaks is indeed difficult, because the Cu 2p peak appears to be attenuated due to surface contaminants/the Zr-based layer and consequently can hardly be used for quantification. Moreover, the calculation model introduced by Hazell et al. [33] is only valid for binary Al-Cu alloy systems, but not for complex layer structures such as the investigated conversion coating. Therefore, the authors employed AES as a second and independent method to validate the obtained findings. In this context, the reported XPS trends of the Zr concentration variation as a function of the initial hydroxyl fraction are fully in line with the Auger Electron Spectroscopy results presented in Figure 4.7.



Figure 4.9: Normalized peak areas for the Zr and Al peaks for the differently treated samples.

Figure 4.10 shows a schematic representation of the effect of the hydroxyl fraction on the deposition of Zr-based conversion layers on AA6014. For the low hydroxyl fractions, thin conversion films with low content of Zr and aluminium rich oxides/hydroxides are obtained. On the other hand, for samples with high hydroxyl fractions, thicker conversion coatings are formed. Regardless of the hydroxyl fraction, the Cu concentration is in the range of 3 and 5 at% within the conversion films.

A comparison of the results presented in this section with those of obtained by Taheri et al. [23] for pure zinc shows that the hydroxyl fraction has a larger impact on the Zr-based conversion coatings deposited on AA6014. For pure zinc samples with hydroxyl fractions between 14 and 25%, Zr is detected by means of AES depth profiles after 3 min of sputtering. A comparison of the normalized Zr peak areas presented in Figure 4.9 with those of Taheri et al. [23] clearly exhibits the drastic effect of surface hydroxyls of AA6014 on deposition of Zr-based conversion films. In the mentioned study, the lowest ratio obtained between the Zr and Zn normalized peak area is around 1.7, while in the present study the lowest ratio obtained between the Zr and Al normalized peak areas is around 0.25.



Figure 4.10: Schematic representation of the effect of the initial hydroxyl fraction on the final Zr-based layers deposited on AA6014.

The effect of the surface hydroxyl fraction in the formation of Zr-based layers can be linked to the first stage of formation of the film, which represents the chemical dissolution of the oxide layer by the free fluorides present in the conversion bath. The chemical dissolution is an ion exchange process between the F^- and O^{2-} , which leads to the formation of an Al-F complex [12]. Upon hydration, the adsorption of free fluorides by surface hydroxides can be represented by the following two step mechanism [34-38]:

$$\underline{\text{Al}}\text{OH}_{(s)}^{+} \text{H}^{+} \rightarrow \underline{\text{Al}}\text{OH}_{2}^{+}$$
(3)

$$\underline{\text{AlOH}}_{2}^{+} + xF^{-} \rightarrow \underline{\text{Al}}F_{x}^{3-x} + H_{2}\text{O}$$
(4)

Once the Al-F complex is formed, it is detached from the surface towards the bulk solution [39, 40]. Pulfer et al. [41] demonstrated that most of the absorbed fluoride ions are exchanged with surface hydroxyl groups. Additionally, Farrah et al. [42] demonstrated that the absorption capacity of aluminium hydroxides is higher than aluminium oxides. Consequently, it can be assumed that the time required for the chemical dissolution of the oxide layer is reduced with increasing the hydroxyl fraction, allowing more time for the Zr-based conversion stage to take place within the preset timeframe.

4.3.3. Open circuit potential evolution during the deposition of Zr-based layers

Figure 4.11 shows the OCP response of the differently treated samples in the Cu-containing hexafluorozirconic acid solution. For the reference sample, the potential initially decreases from - 0.25 V_{SCE} until it reaches a minimum at -0.58 V_{SCE} after 60 s in the conversion bath. Then the potential increases until around -0.38 V_{SCE} in 150 s. In the case of the alkaline treated sample, the potential decays from -0.05 V_{SCE} until -0.48 V_{SCE} after 47 s and then increases until a stable potential of -0.30 V_{SCE} is achieved after 85 s. For the pseudoboehmite treated samples, the potential decreases from -0.10 V_{SCE} until -0.50 V_{SCE} after 70 s, and then constantly increases until -0.30

 V_{SCE} . In the case of the acid treated sample, the potential decreases from -0.15 V_{SCE} until a minimum is achieved at -0.45 V_{SCE} in 120 s, and then the potential only increases 40 mV in the remaining 80 s of measurement. Unlike the rest of the samples, for the thermally treated sample two minimums are observed, one at -0.42 V_{SCE} after 10 s and another one at -0.60 V_{SCE} after 95 s. Then, like for the other samples, the potential increases to -0.35 V_{SCE} after 200 s.



Figure 4.11: OCP responses of the differently treated AA6014 samples in the conversion bath.

The initial decay in the potential is related to the chemical dissolution of the oxide by the free fluorides present in the conversion solution, which is accompanied by a high anodic activity. Throughout this stage in the formation of the conversion film, the aluminium oxide layer is thinned by the free fluorides. As a result, the ionic and electronic conductivity of the oxide film increases. Therefore, the anodic dissolution of the aluminium is enhanced in this part of the process [43]. The reason why the initial decrease in the potential varies with the differently treated samples could be related to fact that the electronic properties of the oxide layer are highly related to the hydroxyl fraction [44, 45]. On the other hand, for the thermally treated sample, two local minimum potential values are observed during the OCP measurement. The first minimum could be related to the initial dissolution of Mg present in the oxide layer.

Subsequently, a local increase in the pH is promoted by the hydrogen ion and oxygen reduction reactions, triggering the deposition of Zr. In the case of the AA6014, cathodic surface intermetallics contribute to an establishment of locally increased pH areas. Additionally, the hexafluorozirconic acid solution used in this study contains Cu^{2+} ions, which accelerate the deposition process of the Zr-based layer upon their local precipitation as metallic Cu, increasing the hydrogen ion and oxygen reduction kinetics [18-20]. The reason why a minimum potential is present in the OCP is a consequence of the high cathodic activity stimulated by the Cu deposition, hydrogen evolution and oxygen reduction reactions. Figure 4.12 shows the time required to reach the minimum in the OCP to the conversion coating surface analysis results presented in section 3.2, it can be concluded that well formed conversion layers are obtained for samples in which the minimum in the OCP is reached in less than 70 s. For the acid and thermally treated samples, the minimum in the OCP is reached in more than 90 s, which is the deposition time used for the ex-situ surface analysis.



Figure 4.12: Time required to reach a minimum in OCP as a function of the hydroxyl fraction.

4.4. Conclusions

This work focuses on studying the effect of the surface hydroxyl fraction prior to the deposition of Zr-based conversion films on AA6014. By means of ex-situ surface analysis, it was shown that higher hydroxyl fractions on AA6014 are beneficial for the formation of Zr-based conversion layers. For samples with hydroxyl fractions of 13 and 22%, less developed conversion layers were obtained, with a high concentration of Al at the surface. For samples with hydroxyl fractions between 46 and 52%, the surface is mostly covered by ZrO₂. The reason of this behavior is most likely related to the first step in the formation of the Zr-based coatings, which consists of the chemical dissolution of the oxide layer by the free fluorides present in the conversion bath. The mechanism of chemical dissolution consists of the formation of an Al-F complex by absorption of the free fluorides, which is later detached from the surface towards the bulk solution. Since the free fluorides mainly interact with the hydroxyl groups, the absorption and detachment process will start relatively early for samples with a higher initial hydroxyl fraction, allowing more time for the deposition stage in the formation timeframe of the Zr-based coating. The variation of the converted layer versus the initial surface composition could have a major effect on the interaction properties of the subsequent organic polymer coating.

4.5. References

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Chapter 5

The effect of surface conditioning treatments on the local composition of Zrbased conversion coatings formed on aluminium alloys

The present work investigates the local elemental distribution of differently treated AA6014 and AA1050 aluminium alloy surfaces before and after the application of Zr-based conversion coatings. To this aim, different surface conditioning treatments were applied before the deposition of the Zr-based conversion films. The Zr-based conversion films were applied by immersion in a hexafluorozirconic acid solution with additions of Cu. Field Emission Auger Electron Spectroscopy was used to study the local composition of the differently treated samples. Surface maps, localized FE-AES spectra and depth profiles were acquired for that purpose. Results have shown the presence of Cu-rich regions regardless of the alloy and surface conditioning treatment.

Keywords: Zr-based conversion coatings, Aluminium alloys, FE-AES, Surface treatments.

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5.1. Introduction

Conversion treatments are commonly employed in the manufacturing process of metallic components to reduce the corrosion susceptibility and to increase the adhesion performance of organic coatings to these substrates [1-9]. The process depends on the transformation of the native oxide layer on the substrate material into a functional coating film, typically due to the precipitation of phosphate crystals or of amorphous metal oxides from solution.

Currently, Zr- and Ti- based thin film technology more and more replaces conventional phosphating due to several advantages regarding costs, easy process control, reduced energy consumption and the avoidance of extensive wastewater treatment protocols. State-of-the-art conversion coating often relies on the properties of hexafluorozirconic acid or hexafluorotitanic acid solution, mediated by diverse functional additives to ensure desired thin film structures on various metals such as steel, galvanized steel and aluminium. The resulting coatings typically achieve a thickness of not more than 20-100 nm and are mainly composed of TiO₂/ZrO₂ [10].

Upon immersion of the metal substrate in the conversion bath, the Zr deposition process starts with the chemical dissolution of the oxide layer by free fluoride. For aluminium alloys, the effectivity of this step is highly determined by the surface chemistry of the oxide layer. In particular, it is strongly dependent on the conditions of any surface pre-conditioning such as acidic, neutral or alkaline cleaning steps which are typically part of the industrial manufacturing processes. For example, Cerezo et al. [11] recently suggested that high hydroxyl fractions on AA6014 favors the chemical dissolution of the oxide layer and significantly impacts the composition of any subsequently precipitated Zr-based conversion coating. Such precipitation is triggered by the local alkalinization of the metal/solution interface and the increase in pH is promoted by oxygen reduction and hydrogen evolution reactions [12-13]. For aluminium alloys, several authors reported that these reactions are predominant on the cathodic intermetallic particles, and therefore the deposition starts at these sites [14-16]. Once a covering film is achieved, an increase in the thickness occurs during longer immersion times [13]. Adhikari et al. [17] used the Quartz Crystal Microbalance to prove that the growth rate of the Zr-based coating on different metals is accelerated by the addition of Copper ions to the conversion bath solution. X-ray Photoelectron

Spectroscopy studies carried out by Lostak et al. [18] confirmed an increase of the film thickness under these conditions. The acceleration mechanism is based on the deposition of Cu by displacement reactions, which provide additional cathodic sites for local alkalinization at the surface. Cerezo et al. [19] reported that the amount of Cu within the conversion film strongly depends on the type of substrate on which the coating is formed. In a recent work, Sarfraz et al. [20] investigated the role of the intermetallics and of copper ions present in a fluorozirconic acid solution for the deposition of Zr-oxide based coatings on alkaline pre-conditioned AA6014 surfaces. A preferential deposition of Cu on top of the intermetallics present at the surface was proven and emphasized the locally inhomogenous structure of conversion layers on aluminium.

The present study extends this approach. Determined by the type of Al alloy, Cu is already present in the aluminium matrix and/or part of the elemental composition of the intermetallic particles. Prior to an immersion in the conversion solution, alkaline and/or acidic surface conditioning treatments are commonly applied to remove organic contaminants. Thereby, aged oxide films are removed by freshly grown oxide layers which also exhibit specific reactivity towards subsequent conversion coating. During this process, the local elemental composition on the substrate surface gets modified in the micron and sub-micron range. Depending on the type of pre-conditioning, a release of functional species will occur, which may result in an additional source for Cu crystallization cores across the substrate surface. In other words, it has to be expected that the cleaning stage prior to the conversion treatment will pre-determine the distribution and a possible local enrichment of active Cu sites. Those sites, in turn, will impact the subsequently generated Zr-oxide layer structure as well as its thickness.

Unfortunately, such effects were not investigated in detail so far. As a consequence, potential optimizations of the related industrial manufacturing processes were not exploitable up to now. In this context, the present publication will provide a significant contribution to a better understanding. Therefore, different model surface conditioning treatments were applied on pure Al and different Al alloys prior to the immersion in a Cu-containing hexafluorozirconic acid solution. Field Emission Auger Electron Spectroscopy (FE-AES) was used to acquire high-resolution surface maps, localized spectra and depth profiles as well as to characterize the elemental distribution of the specimens before and after the formation of the Zr-based conversion

coatings.

5.2 Experimental

Sheets of AA6014 and AA1050 aluminium alloys provided by Henkel AG & Co. KGaA and Goodfellow respectively were used in this study. AA6014 contains Mg ≤ 0.8 wt.%, Fe ≤ 0.35 wt.%, Si ≤ 0.6 wt.%, Cu ≤ 0.2 wt.%, Mn ≤ 0.2 wt.% as alloying elements. On the other hand, AA1050 is composed of Al \geq 99.5 wt%, Fe ≤ 0.3 wt.%, Si ≤ 0.2 wt.%. All the specimens were mechanically ground with SiC paper and polished in subsequent steps to different grade diamond paste (9, 6, 3, 1, and 0.25 µm). Then, the samples were ultrasonically degreased in ethanol for five minutes and dried in compressed air. Subsequently, the from now on called reference sample was exposed to an acid, alkaline or thermal treatment. The acid treatment was composed of the immersion of the samples for 30 s in a 30 vol.% nitric acid solution. This was followed by 3 min rinsing in deionized water and drying with compressed air. For the alkaline treatment, the samples were dipped in a 3 vol.% potassium hydroxide solution at 57 °C with a stirring rate of 150 rpm for 3 min. The pH of this solution was adjusted to 10.8 at 57 °C with phosphoric acid at 10 vol.%. For the thermal treatment the specimens were heated in air at a temperature of 275 °C for 24 h.

To form Zr-based conversion coatings, samples were dipped into a modified hexafluorozirconic acid solution (Zr < 200 mg/l) that included smaller amounts (< 50 mg/l) of non-hazardous components of Cu [17, 19] provided by Henkel AG & Co. KGaA. Treatment occurred in a 1L-beaker during 90 s in stirred solution (employing a stirring bar at 400 rpm) with a pH of 4 (adjusted by 15 vol% ammonium bicarbonate). Afterwards, the samples were rinsed with deionized water and dried with compressed air.

The surface analysis before and after the formation of the Zr-based conversion coating was conducted with a JEOL 9500F JAMP Scanning Auger Microprobe. For that purpose, an electron beam of 10 kV, 1 nA and 8 nm in diameter was applied at an angle of incidence of 30° with respect to the sample surface normal. When carbon was detected at the surface, the sample was sputtered with 1 KeV Ar⁺ ions to remove the contamination. Scanning Electron Microscopy (SEM) images of the studied area were acquired using a secondary and a backscattered electron detector attached

to the FE-AES system. For all the samples, localized FE-AES spectra were acquired in different zones. Surface maps were recorded establishing the color scale of the map as the intensity ((peak-background)/background) for each element. Additionally, depth profiles were obtained using argon sputtering at an energy level of 1 keV. The data were processed using the JEOL Image and Spectra Investigator software. Since the sputter rate related to the chemical composition and morphology of the matrix, the depth is presented as a function of the sputter time.

5.3. Results and discussion

5.3.1. FE-AES study of acidic and alkaline treated AA6014 samples

To study the local composition of the AA6014 specimen after the application of the surface conditioning treatments, FE-AES spectra were acquired on the different samples. Figure 5.1 a) presents a SEM micrograph of the studied area of the reference sample. As observed, several bright particles are present at the surface, with a size of less than 1 μ m². Figure 5.1 b) shows FE-AES spectra acquired on such a particle (area 1) and on a particle free zone of the surrounding Al matrix (area 2). The area 1-spectrum exhibits three peaks between 590 and 700 eV, which refer to Fe LMM transitions, and predominant signals around 1350 eV, which reflect Al KLL transitions. In the area-1 spectrum, the iron signals are missing and mainly Al is detected. It should be generally noticed that no traces of Cu were detectable on the surfaces of the pure Al reference samples.





Figure 5.1: a) SEM micrograph of the AA6014 reference sample. b) Localized FE-AES spectra at two different zones of the sample.

Figure 5.2 a) shows a SEM micrograph of the AA6014 alkaline treated specimen. As observed, the surface contains several rounded particles of 500 nm or less in diameter. FE-AES spectra were acquired inside and outside of these particles and the results are presented in Figure 5.2 b). The areas in which the FE-AES spectra were acquired are indicated in Figure 5.2 a). The FE-AES spectrum taken on the particle shows the presence of three peaks between 780 and 930 eV, which correspond to the Cu LMM transition. These signals clearly indicate a Cu-enrichment at the substrate surface and thereby confirm a release of copper species from the Al-alloy matrix and/or the embedded intermetallic particles during an immersion in alkaline solution.



Figure 5.2: a) SEM micrograph of the AA6014 alkaline treated specimen. b) FE-AES spectra at two different areas of the specimen.

The FE-AES analysis of the acidic treated AA6014 sample is presented in Figure 5.3. Figure 5.3 a) shows an SEM image of the overall investigated area. Marked zones refer to locations on which FE-AES spectra were acquired. In general, an intermetallic particle of $2x2 \mu m$ in size can be easily identified. On top of the intermetallic phase as well as in its vicinity, distinctly smaller and bright particle 'dots' seem to be distributed. Figure 5.3 b) presents three FE-AES spectra recorded on the Al matrix (area 1), on a 'dot-free' zone of the intermetallic (area 2) and on one of the small bright particles (area 3). For area 1 majorly Al is detected (see the Al KLL peak), whereas the sample surface in area 2 mainly consists of iron (see the Fe LMM transitions). Interestingly, a significant amount of Cu is detected on the small particle dots in area 3 (see the Cu LMM signals).The
presence of Cu-rich particles for the alkaline and acid treated specimens combined with the lack of Cu at the surface for the reference sample suggest a de-alloying process as a result of these surface conditioning treatments. It is important to note that conventional energy dispersive X-ray spectroscopy would indicate the presence of copper even for the reference sample due to its large penetration depth of several μ m. FE-AES, in contrast, is extremely surface sensitive and just probes the first few nm of the sample – relevant Cu amounts hidden in the Al matrix beneath this surface layer will not contribute to the detected elemental composition.



Figure 5.3: a) SEM micrograph of the AA6014 acid treated samples. b) FE-AES spectra at three different zones of the specimen.

FE-AES consequently shows that during immersion in acidic and alkaline solutions, initial dissolution of Cu-rich intermetallic particles occurs, followed by a re-deposition of Cu clusters around and further outside the site of origin due to the solution movement [21]. This Cu enrichment has been previously reported by Dimitrov et al. [22] for Al-Cu-Mg alloys that were in contact with alkaline solutions. Several authors have also shown the presence of Cu at the surface of different aluminium alloys after the exposure in acid solutions [23-26]. In this context, etching of the alloy surface in alkaline or acidic solution is an important prerequisite, because only the dissolution of a few nanometers of the Al matrix will excavate a relevant amount of intermetallics at the substrate surface, which can be subsequently subject to de-alloying [26]. Figure1 confirms this, because without etching, no Cu-rich intermetallics are detected.

5.3.2. FE-AES study of the Zr-based conversion coatings deposited on the acidic and alkaline treated aluminium alloys

To study the local elemental distribution of the Zr-based conversion coatings formed on the differently pre-conditioned aluminium alloys, FE-AES spectra, depth profiles and elemental maps were acquired. Figure 5.4 a) shows a SEM micrograph of the AA6014 alkaline treated specimen after immersion in the conversion bath. Different bright rounded particles of 500 nm or less in diameter are observed. Figure 5.4 b) presents FE-AES spectra that were acquired on these particles (area 1) and on the surrounding Al matrix (area 2). For both zones, Zr, Al, O and C are detected. The intensities of the different transitions for these elements are similar in both areas. Remarkably, Cu is only present on the bright areas. Figure 5.5 shows FE-AES maps for Zr, Al and Cu that were recorded in the area of the SEM image of Figure 5.4 a). These maps confirm a homogeneous distribution of Zr and Al, while Cu seems to be locally enriched in the form of agglomerates. It is clear that the Cu-rich zones correspond to the bright zones of Figure 5.4 a). Based on the findings discussed in the previous section, the formation of Cu dots has to result from both de-alloying/redeposition processes of Cu ions during alkaline cleaning and additional precipitation of Cu-ions from the subsequently generated conversion coating layer. Comparing Figure 5.2 a) with Figure 5.4 a), the number of detectable Cu agglomerates does not seem to increase significantly by immersion in the conversion coating solution, however, their average size, in fact, does.



Figure 5.4: a) SEM micrograph of the Zr-based conversion coating deposited on the AA6014 alkaline treated specimen. b) FE-AES spectra at two different areas of the sample.





Figure 5.5: FE-AES a) Zr, b) Al, c) Cu map of the Zr-based conversion coating formed on the AA6014 alkaline treated sample.

FE-AES depth profiles were recorded in zones with (Figure 5.6 a)) and without the Cu enrichment (Figure 5.6 b)) to study the film compositions in more detail. Zr, O, Al and C are predominant elements in both areas, but the layer structures nevertheless distinctly differ. A significant amount of Cu is only verifiable in Figure 5.6 a). Its maximum is achieved at around 16 at% after about 2 min of sputtering, then slowly decays. The data point at a distribution of Cu throughout the entire conversion film with no specific enrichment at the interface between substrate and conversion layer. In Figure 5.6 b), the amount of Zr decreases to half of its maximum value after 1 min of sputtering, whereas for Figure 5.6 a), such decrease is not detected before 2 min of sputtering. This indicates that the thickness of the conversion film in Cu-rich zones is at least two times higher than the one obtained in regions without Cu deposits. Regarding the chemical state of the Cu agglomerates, FE-AE spectra do not indicate any change of oxidation states throughout the conversion layer. Figure 5.7 presents Cu LVV peaks recorded in the Cu-rich zones of Figure 5.6 a) after 0.5 and 2.5 min of argon sputtering, which refers to signals recorded near the outer surface of the Zr-oxide layer and those obtained near the interface to the substrate. Both peaks exhibit very similar shapes with an intensity maximum at 914 eV. They can be assigned to CuO [28, 29] and confirm the results discussed by Sarfraz et al. [20]. Currently, it is not clear whether an initial oxidation of metallic Cu occurs in the course of conversion layer formation or rather reflects an artifact resulting from sputtering during layer analysis [30].



Sputter time [min]



Figure 5.6: Localized FE-AES depth profiles of the Zr-based conversion film deposited on the AA6014 alkaline treated specimen on a) a Cu-rich zone and b) a zone without Cu.



Figure 5.7: Cu LVV spectra recorded at different depth of a Cu-rich zone of the Zr-based conversion film formed on the alkaline treated AA6014 specimen.

Figure 5.8 a) presents a SEM micrograph of the Zr-based conversion coating deposited on the AA6014 acidic treated specimen. Like in the case of the alkaline treated sample, it shows bright rounded shaped particles of 500 nm or less in diameter. FE-AES spectra were acquired on these particles and the surrounding Al matrix. Figure 5.8 b) shows that Zr, Al, C and O are verifiable in both regions, while Cu is only detected on the bright particle. Similar to the results shown in Figure 5.4 b), the intensities of the Zr and Al peaks are similar for both of the studied regions. Figure 5.9 shows the corresponding FE-AES Zr, Al and Cu maps obtained for the surface section analyzed in Figure 5.8. Similar to the alkaline treated specimen, all elements except the Cu are homogeneously distributed over the surface. Remarkably, the density of Cu-rich particles is distinctly higher. This finding clearly indicates that the amount of actively growing Cu-crystallization cores during conversion coating formation can be specifically tailored based on the type of pre-conditioning and cleaning.



Figure 5.8: a) SEM micrograph of the Zr-based conversion film formed on the acid treated AA6014 specimen. B) FE-AES spectra of two different areas of the sample.





Figure 5.9: FE-AES a) Zr, b) Al, c) Cu map for the acid treated AA6014 aluminium alloy.

Figure 5.10 presents the FE-AES Zr, Al and Cu maps together of with SEM image of the studied area for Zr-based conversion layers formed on the AA1050 alkaline treated specimen. Like in the case of the acidic and alkaline treated AA6014, a homogeneous distribution of Zr and Al is obtained, while Cu precipitated inhomogeneously so that Cu-rich areas are observed for this sample, as well. Since the AA1050 is a Cu-free aluminium alloy, all Cu particles observed on Figure 5.10 c) have to result from precipitation from the conversion coating solution.





Figure 5.10: FE-AES a) Zr, b) Al and c) Cu map of the Zr-based conversion coatings deposited on the AA1050 alkaline treated sample. d) SEM micrograph of the studied area.

5.3.3. FE-AES surface morphology study of thermally pre-conditioned AA6014

To further explore the importance of the Al-oxide layer structure on the interdependency of Cu precipitation and Zr-deposition kinetics during conversion coating, additional experiments were performed with thermally conditioned samples. Figure 5.11 a) presents a SEM micrograph of a thermally treated AA6014 specimen. Different bright spots are observed on its surface. FE-AES spectra shown in Figure 5.11 b) were acquired on these spots (area 1) as well as on the surrounding Al matrix (area 2). For area 2, mainly aluminium and oxygen signals were recorded, whereas additional peaks were recorded in the spectrum of area 1. With an energy of approximately 1150 eV and 1550 eV, they refer to Mg and Si KLL transitions and confirm an enrichment of magnesium and silicon at the surface due to their preferential oxidation at elevated temperatures during thermal treatment [27].





Figure 5.11: a) SEM micrograph of the AA6014 thermally treated specimen. b) FE-AES spectra at two different locations of the sample.

Figure 5.12 a) presents a SEM micrograph of a thermally treated AA6014 sample after immersion in the conversion solution. Several round shaped particles of approximately 1 \Box m in diameter are present at surface. Figure 5.12 b) shows the FE-AES spectra acquired on one of the bright particles (area 1) and of the Al matrix (area 2). For area 1, Al KLL, Cu LMM and O KLL peaks appear in the spectrum, whereas no copper signals were obtained from area 2. As no de-alloying effects were observed on AA6014 after thermal pre-conditioning of the surface so that no Cu was precipitated, the conversion coating bath itself will be the only source for Cu deposition in the present case. Interestingly, no or almost no Zr is verifiable on the surface [11]. A similar observation was made

for the thermally pre-conditioned sample presented in Figure 4. This means that any preferential film formation effects for Zr-based conversion layers that may be mediated by Cu crystallization cores will be suppressed if a relatively thick and compact oxide layer on the Al alloy is formed during exposure to elevated temperatures before. This is an important observation, as Al-compounds can be subject to heat treatment procedures prior to thin-film deposition in the course of industrial manufacturing processes.



1000 Kinetic energy [eV]

1500

2000

Figure 5.12: a) SEM micrograph of the Zr-based conversion coating formed on the AA6014 thermally treated specimen. b) FE-AES spectra at two different areas of the sample.

500

0

5.4. Conclusions

The effects of alkaline, acidic and thermal pre-conditioning treatments for AA6014 were investigated with respect to the layer characteristics of subsequently precipitated Zr-based thin film conversion coatings. Complementary data were obtained on pure Al and copper-free AA 1050 surfaces. The following conclusions can be drawn:

→ Immersion of copper-containing AA6014 in acidic and alkaline solution results in de-alloying of embedded intermetallics particles, which results in dissolution and re-distribution of Cuagglomerates on top of the intermetallics and across the surface of the surrounding Al matrix. As a result, active Cu crystallization cores are already present at the sample surface when it is immersed in Cu-containing hexafluorozirconic acid solution. During conversion coating, the Curich particles do not seem to grow significantly in number, but in size. At and around the Cuenriched zones, the resulting conversion coating thickness consequently occurs to be significantly increased, whereas the Zr amount was rather homogeneously distributed across the surface.

 \rightarrow De-alloying only occurs if the pre-conditioning procedure induces etching of the AA6014 alloy surface. Any thickening or compaction of the oxide layer due to thermal treatment inhibits the conversion layer formation. In that case, the conversion bath solution itself functions as the only source for Cu precipitation, but even under these conditions hardly any Zr deposition can be induced.

 \rightarrow If Cu is absent in the AA alloy, in particular for AA1050, etching of the substrate surface, e.g. due to alkaline pre-conditioning, does not only allow for subsequent Cu deposition from the conversion bath solution, but also enables a correlated precipitation of zirconium species.

In general, it is shown that pre-conditioning/cleaning procedures on Al compounds allow specific control and adjustment of the distribution of Cu agglomerates on the surface. These Cu-rich zones have a strong impact on the local thickness of the conversion coating, but cannot stimulate the Zr deposition process if the surrounding Al oxide structure was not adequately activated before.

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Comparison of the effect of surface hydroxyls on the formation of Zr-based conversion coatings on different metals

The development of environmentally friendly conversion coatings for the automotive industry as a replacement of the traditional phosphating system is an important research topic nowadays. Given the relevance of this subject, a new generation of conversion coatings formed after immersion in a dilute Cu-containing Zr-based conversion solution was employed in this study. This particular work is focused on the effect of the surface conditioning treatments on the formation of Zr-based conversion coatings on cold rolled steel. To promote the formation of oxides layers with different hydroxyl fractions and similar thicknesses different model surface conditioning treatments were applied prior the immersion of the substrates in the conversion solution. X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) depth profiling were used to evaluate the surface chemistry, in-depth distribution and film thickness before and after the formation of the Zr-based conversion coating. The Open Circuit Potential (OCP) during the immersion in the conversion bath was also recorded in order to follow in-situ the electrochemical reactions involved in the deposition of the coating on the differently treated samples. The results presented in this work have shown that the hydroxyl fraction does not have an significant effect on the formation of Zr-based conversion coatings on cold rolled steel. Furthermore, to have overall assessment of the influence of this variable on the formation of Zrbased conversion coatings on different metals, the results presented in this work were also compared to ones already reported for pure zinc and AA6014 aluminium alloy.

Keywords: Zr-based conversion coatings, hydroxyl fraction, cold rolled steel, AA6014, pure zinc

6.1. Introduction

The application of an ultra-thin conversion coating on metallic substrates is commonly used as manufacturing process to improve the corrosion resistance of the metal surface and also the adhesion performance of the subsequently applied organic coating [1-7]. Phosphate containing conversion treatments have been used in the automotive industry for that purpose. Nevertheless, this treatment has several disadvantages. Typically, phosphating baths operates between 35 and 50°C, increasing the cost of the process. Phosphate discharges from the concentrated conversion solution also have a negative impact on ground waters. Another drawback is the large amount of sludge generated in the process. In addition, a sealing step is often required to reduce the porosity of the conversion coating. For these reasons, new environmentally friendly conversion treatments need to be developed without compromising the performance of the coating. Among the different alternatives, the Zr-based conversion coatings, formed by immersion in a hexafluorozirconic acid solution are currently recognized as a suitable replacement [5, 7].

The formation of the Zr-based conversion coating can be divided in different steps, and this process has been described in detail by many authors [8-20]. During the first seconds of immersion in the conversion solution, the oxide layer is thinned and possibly removed, helping the electron tunneling and metal ion migration to take place [21, 22]. Subsequently, the deposition of the Zr-based conversion film begin as a result of a local alkalinization at the metal/solution interface, which is promoted by the hydrogen evolution and oxygen reduction reactions [8-11, 14]. In the particular case of aluminium alloys, several studies have shown that the formation of the Zr-based conversion coatings starts on top of the cathodic intermetallic particles [8-10]. Once these cathodic particles are covered, the deposition continues on the rest of the surface. For longer immersion times an increase in the thickness of the conversion coating is expected [9]. In recent studies, Adhikari et al. [18] and Lostak et al. [20] proved that addition of Cu species to the conversion solution accelerates the formation of the Zr-based conversion coating. The acceleration mechanism is based in the deposition of Cu particles on the surface, which act as additional cathodic sites for the local alkalinization required for the formation of the Zr-based conversion film.

Surface conditioning treatments used before conversion treatment in order to remove contaminant that might interfere with the formation of the film. This treatment however, could modify the chemistry and/or thickness of the metal oxide [23, 24]. Studies on pure zinc [25] and aluminium alloys [26] have shown that the surface hydroxyls on metal surfaces have a important effect on the formation of the Zr-based conversion coatings. To have an overall picture of the influence of this variable on different metals, this work is partially centered in assessing the effect of the surface hydroxyls on the deposition of Zr-based films on cold rolled steel. To achieve this goal, the approach implemented in our previous studies [25-26] was mimicked. Different model surface conditioning treatment were selected and subsequently applied in order to obtain oxide films with different hydroxyl fractions and similar thicknesses prior the deposition of the Zr-based conversion layer. X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) depth profiles were used to characterize the surface chemistry and in-depth distribution of the differently treated specimens before and after the formation of the conversion coating. Additionally, Open Circuit Potential measurements (OCP) were performed during the conversion treatment in order to follow the electrochemical reactions throughout the formation of the Zr-based conversion coatings. Finally, to summarize the effect of the surface hydroxyls on different substrates, the results shown in this work were compared with our previous studies on pure zinc and AA6014 aluminium alloy.

6.2. Experimental

6.2.1. Materials and sample preparation

Panels of cold rolled steel (C \leq 0.1 wt%, Mn \leq 0.50 wt%, P \leq 0.030 wt%, S \leq 0.035 wt%, balance Fe) supplied by Henkel AG & Co. KGaA were used in this study. The samples were mechanically ground with SiC paper (500, 800 and 1200 grid) and subsequently polished with diamond paste (9, 6, 3, 1 and 0.25 µm) to obtain a mirror-like finish. Then, the specimens were ultrasonically degreased in ethanol for 5 min. From now on, the set of samples tested after this step is referred as reference. The metal oxide was then modified by applying an alkaline, carbonate or thermal surface conditioning treatment. The so-called alkaline treatment consisted in the immersion of the specimen in a 3 vol.% potassium hydroxide solution at 57 °C with stirring rate of 150 rpm for 3

min. The pH of this particular solution was adjusted to 10.8 at 57 °C with phosphoric acid at 10 vol.%. The so-called carbonate treatment was applied by immersing the sample in a 0.1 M NaHCO₃ solution at 50 °C for 3 min. The pH of this solution was adjusted to 10 at 50 °C using a 1 M sodium hydroxide solution. Finally, the so-called thermal treatment consisted in heating the samples in air for 8 min at a temperature of 250 °C. The Zr-based conversion coatings were formed by immersing a set of the differently treated samples in a hexafluorozirconic acid solution (Zr < 200 mg/l) with small amount of non-hazardous components of Cu supplied by Henkel AG & Co. KGaA with a stirring rate of 400 rpm [18, 19]. The pH of the conversion solution used in this work was equal to 4, and this value was adjusted using ammonium bicarbonate at 15 vol%. The immersion time used to prepare the specimens for the ex-situ surface analysis was 90 s.

6.2.2. Surface characterization

XPS analysis was conducted using a PHI-5600ci to evaluate the surface chemistry of the treated specimens. The pressure of the analysis chamber was kept at approximately 1×10^{-9} Torr. The peaks were recorded using a monochromatic Al K α source (1486 eV) with a pass energy of 23.5 eV and 0.1 eV step size. These measurements were performed using a take-off angle of 45° with respect to the sample surface. The peak fitting was performed using the PHI Multipak V8.0 software, using a Shirley-type background removal and a mixed Gauss-Lorentz shapes. Before starting with the fitting of these peaks, the spectra were shifted to set the C-C/C-H component of the C 1s peak at a binding energy of 284.8 eV to correct the sample charging [27].

Auger Electron Spectroscopy (AES) depth profiles were acquired to investigate the in-depth elemental distribution and film thicknesses of the differently treated cold rolled steel specimens. For that purpose, a PHI 650(SAM) with a LaB6 cathode and a Cylindrical Mirror Analyzer (CMA) was used. Throughout the experiments, the base pressure in the analysis chamber was kept at approximately $3x10^{-10}$ Torr. A primary electron beam with an energy of 5 keV and an emission current of 1 µA incident on the sample surface at 30° to the normal was used. Ion sputtering was performed using 5 keV Ar⁺ ions, with an Ar⁺ pressure of 10 mPa and an emission current of 20 mPa. The ion beam was used at intervals of 1 minute and impinged on the sample surface at 50° to the normal. The recorded spectra were processed and analyzed with the PHI-Multipak software

V8.0. All the measurements carried out in this section were repeated three times in order to verify the reproducibility.

6.2.3. Open circuit potential during the deposition of Zr-based conversion layers

A Solartron SI 1287 potentiostat and a Saturated Calomel reference Electrode (SCE) were used to record the Open Circuit Potential (OCP) for 200 s during the immersion of the cold rolled steel panels in the conversion bath. The potential value was recorded every 1 s. All potentials presented in this work are given vs. SCE electrode. For all the specimens, the standard deviation after repeating the experiment three times was in the order of 7 mV. Therefore, the OCP results presented in this study are considered reproducible.

6.3. Results and discussion

6.3.1. Surface characterization of the differently treated cold rolled steel samples

The hydroxyl fractions for the differently treated cold rolled steel specimens were obtained using the model proposed by McCafferty et al. [23]. Figure 6.1 presents the average calculated hydroxyl fraction for the differently treated specimens. As shown in Figure 6.1, the thermally treated sample had the lowest hydroxyl fraction, with 13%. The second lowest hydroxyl fraction is seen for the alkaline treated specimen with 22%. For the carbonate treated sample and reference sample, the calculated hydroxyl fractions were 29 and 40% respectively. The standard deviation for this calculation was 2% or less, depending on the treatment. The values obtained for the alkaline and thermally treated samples are in the same order of magnitude to the ones reported by Wieland et al. [28] for similar treatments on interstitial free DC06 steel.



Figure 6.1:Calculated hydroxyl fraction for the differently treated cold rolled steel specimens.

AES depth profiles were acquired to verify that the oxide film thickness of the different treated samples was similar. For that purpose, the model proposed by De Laet et al. [29] was used. According to this model oxide film thickness is defined as the sputter time required to increase the Al KLL peak intensity to 50% of its maximum value. The average calculated oxide film thickness is presented in Figure 6.2. As observed in Figure 6.2, the differences between the oxide film thickness of the differently treated specimens are really small (less than 10%).



Figure 6.2: Calculated oxide layer thickness of the differently treated cold rolled steel samples.

6.3.2. Surface characterization of the Zr-based conversion coatings formed on the differently treated cold rolled steel samples

AES depth profiles of the Zr-based conversion layers formed on the differently treated cold rolled steel specimens are presented in Figure 6.3. The two major elements detected during the first minutes of sputtering are Zr and O. In this part of the films, only a small amount of Fe in order of 3 at% is detected. This indicates that for the different hydroxyl fraction obtained in this study, well-defined Zr-based conversion layers are obtained on the cold rolled steel substrates. After 3 min of sputtering, the Fe content starts to increase, until 95-99 at% is reached after 12 min of argon sputtering. This smooth increase in the Fe content is partially related to the argon sputtering. After certain sputtering time the film is fully removed by the argon in some sites, while in other places the coating is still present. Fluorine is also detected at the surface of all the specimens, with a maximum content of 3-4 at%, which rapidly decays with the argon sputtering. Cu is also observed within the conversion films. The maximum Cu content for all the treated specimens was between 8 and 10 at% and this maximum is seen after 4 to 6 min of argon sputtering. Since the difference between the maximum Cu content is close of the detection limit of the equipment, no correlation between the hydroxyl fraction and the Cu deposition can be extracted from these results. On the other hand, if the maximum Cu content seen in the AES depth profiles is compared to the ones presented by Cerezo et al. [26] for AA6014 aluminium alloys, it can be noticed the amount of Cu in the conversion films deposited on cold rolled steel is two times higher.





Figure 6.3: AES depth profiles of the Zr-based conversion layers deposited on the a) alkaline treated, b) carbonate treated, c) reference and d) thermally treated samples.

The maximum concentration of Zr recorded by means of AES depth profiles for the Zr-based conversion coatings deposited on the differently treated specimens is presented in Figure 6.4. The calculated hydroxyl fraction for each specimen before the formation of the Zr-based conversion films is also indicated. For all the samples, the maximum Zr content is the same, regardless of the hydroxyl fraction. Figure 6.5 presents the Zr-based conversion coatings thicknesses of the differently treated specimens, measured by AES depth profiles. These thicknesses were obtained using the model introduced by Campestrini et al. [30], which defines the film thickness as sputter time required to decrease 50% of the intensity of Zr peak. As observed in Figure 6.5, the thicknesses of the Zr-based conversion coatings are also very similar regardless of the surface conditioning treatment. The thicknesses presented in Figure 6.6 are equivalent to 60 nm. This approximation was obtained by measuring the depth of the crater after 1 min of argon sputtering using Atomic Force Microscopy (AFM). From this test, it was obtained that the depth of the crater was in the order of 10 nm. Combining this sputter rate with the results presented in Figure 6.5 the real thickness of the films was estimated.



Figure 6.4: Maximum concentration of Zr detected by means of AES depth profiles for the Zr-based films deposited on the differently treated cold rolled steel specimens.



Figure 6.5: Calculated Zr-based conversion coating thickness of the differently treated samples.

In order to compare the effect of the hydroxyl fraction on the deposition of Zr-based conversion films on different metals, Figure 6.6 presents the thicknesses of the conversion coatings deposited on AA6014 aluminium alloy, cold rolled steel and pure zinc on specimens different hydroxyl fractions. The results presented in Figure 6.6 combines the data presented in this work with the one reported by Taheri et al. [25] for pure zinc and by Cerezo et al. [26] for AA6014 aluminium alloy. The data shown in Figure 6.7 only includes the results obtained for the specimens with the lowest and highest hydroxyl fractions obtained in each work, and the value obtained for the hydroxyl fractions are also indicated. As observed in Figure 6.6, the thinnest Zr-based conversion layer is obtained for low hydroxyl fractions on AA6014, followed by the films deposited on AA6014 with high hydroxyl fraction. On the other hand, the coatings formed on pure zinc and cold rolled steel are more than two times thicker than the ones formed on AA6014, regardless of the hydroxyl fraction.



Figure 6.6: Comparison of the effect of the hydroxyl fraction on the resulting Zr-based conversion coatings thickness for AA6014, cold rolled steel and pure zinc [25, 26].

To further study the effect of the surface hydroxyls on the formation of Zr-based conversion coatings on cold rolled steel, XPS analysis was conducted on the differently treated samples after immersion in the conversion bath. To compare the relative amount of Zr deposited with respect to the Fe for the differently treated specimens, the peak areas of the fitted Zr 3d, Fe 2p and Fe 3p peaks were studied. Using a similar procedure to the ones implemented by Taheri et al. [25] and Cerezo et al. [26] for XPS data processing, the following normalization factors were introduced to subtract the experimental variations generated by the differences between the sample position and X-ray source and detector:

$$\Delta Zr = \frac{Zr \ 3d \ area}{Zr \ 3d \ area + Fe \ 2s \ area + Fe \ 3p \ area}$$
(Eq. 1)
$$\Delta Fe = \frac{Fe \ 2s \ area + Fe \ 3p \ area}{Zr \ 3d \ area + Fe \ 2s \ area + Fe \ 3p \ area}$$
(Eq. 2)

Figure 6.7 shows the average of these normalization factors calculated using Eq. 1 and Eq. 2 for the films formed on the differently treated cold rolled steel specimens. According to Figure 6.7, the relative content of Zr with respect of Fe measured by XPS are very similar independently of the hydroxyl fraction. The information extracted from Figure 6.7 concerning to the Zr normalization factor is in agreement with the AES results reported in Figure 6.4. Moreover, the

relative amount of Fe measured by XPS for the conversion coatings deposited on the differently treated specimens is also low, which is also in accordance with the AES depth profiles shown in Figure 6.3. On the other hand, Figure 6.8 presents a comparison of the relative amount of Zr with respect to base metal for conversion films deposited on AA6014, cold rolled steel and pure zinc samples with low and high hydroxyls fractions. The results shown in Figure 6.8 combines part of the data presented in Figure 6.7 with the one reported by Taheri et al. [25] for pure zinc and by Cerezo et al. [26] for AA6014. The results presented in Figure 6.8 only include the results obtained for the specimens with the lowest and highest hydroxyl fractions obtained in this work and in the cited studies, and the value obtained for the hydroxyl fractions in each study are also indicated. As observed in Figure 6.8, for all the specimens except for the AA6014 with 13% of hydroxyl fraction, the normalized Zr peak area is above 0.8.



Figure 6.7: Normalized peak areas for the Zr and Fe peaks for the differently treated cold rolled steel samples.



Figure 6.8: Comparison of the normalized Zr peak area for Zr-based conversion coatings deposited on different metals with different hydroxyl fractions [25, 26].

The reason why the hydroxyl fraction has a larger impact in the deposition of the Zr-based conversion coatings on AA6014 in comparison to cold rolled steel and pure zinc is linked in great part to the initial stage of the formation of the film. As explained by Cerezo et al. [26], high hydroxyl fractions on AA6014 are beneficial for the formation of Zr-based conversion films because less time is required for initial stage in the formation of the film, which is the dissolution of the oxide layer. Therefore more time is available for the deposition step for high hydroxyl fractions. At a pH of 4, which is the one used in that study, the oxide layer on AA6014 is stable in the absence of complexing agents [33, 34]. As a a consequence, the dissolution kinetic depends entirely on the interaction of the oxide film with the free fluorides, which depends on the surface hydroxyls [35-42]. For cold rolled steel and pure zinc in solution with a pH of 4, the oxide layers are unstable [34, 43-46]. Strehblow et al. [47] showed that for iron immersed in solution at this pH the dissolution of the oxide layer occurs very rapidly, and this process is drastically accelerated if free fluorides are added in the solution. Taking this into consideration, for the time frame used for the ex-situ surface analysis (90 s), the dissolution stage for cold rolled steel and pure zinc occurs so rapidly that there is enough time for the formation stage.

6.3.3. Open circuit potential during the deposition of Zr-based layers

The evolution of the OCP values in the conversion bath for the differently treated cold rolled samples is presented in Figure 6.9. The hydroxyl fraction for each specimen before the immersion in the conversion solution is also indicated. The OCP trend for all the specimens is very similar regarding of the surface conditioning treatment. First, the potential rapidly decreases until a minimum is found. Then the potential slightly increases until a plateau is reached. For the alkaline treated sample, the potential initially decays from -0.1 V_{SCE} until -0.48 V_{SCE} in 50 s and then increases until -0.46 V_{SCE} after 85 s. On the other hand, for the carbonate treated sample, the potential drops from -0.2 V_{SCE} until -0.52 V_{SCE} in 35 s and then increases until -0.50 V_{SCE} in 70 s. For the reference sample, during the first 15 s of immersion the potential drops from -0.3 V_{SCE} until -0.47 V_{SCE} and then slowly increases until a stable potential of -0.45 V_{SCE} is reached after 60 s. Finally, for the thermally treated sample, the potential drops from -0.3 V_{SCE} in 80 s.



Figure 6.9: OCP responses of the differently treated cold rolled steel specimens in conversion solution.

The decrease in potential during the first seconds of immersion indicates a high anodic activity in the initial part of the deposition process. This anodic activity is accompanied by the dissolution of the oxide film, which enhance the electrochemical reactions such as the anodic dissolution of the metal, hydrogen evolution and oxygen reduction reactions. As observed in Figure 6.9, the initial decay in the potential varies with the surface conditioning treatment. In fact, the potential decrease is less steep as the hydroxyl fraction is reduced. This occurs because the electronic properties of the oxide film are correlated to the hydroxyl fraction [48-49]. The minimum in the OCP is a consequence of the cathodic activity promoted by the Cu deposition, hydrogen evolution and oxygen reduction reactions, which triggers the formation of the film [19]. When a stable potential is reached, it is believed that the surface has been completely covered by the conversion film [9]. As indicated in Figure 6.9, for all the specimens, a stable potential has been reached after 90 s. This means that regardless of the hydroxyl fraction all the cold rolled steel specimens should be completely covered. This information match with the ex-situ surface analytical results presented in Section 3.2.

Figure 6.10 shows a comparison of the potential recorded after 90 s of immersion in the conversion for AA6014, cold rolled steel and pure zinc specimens with low and high hydroxyl fractions. The results for AA6014 and pure zinc were extracted from the data presented by Cerezo et al. [26] and Taheri et al. [25]. For cold rolled steel and pure zinc, the observed differences in the potential after 90 s of immersion in the conversion solution are less than 2 mV_{SCE}. For the AA6014, the difference in the potential between samples with low and high hydroxyl fraction is almost 0.3 V_{SCE}. These results have can be correlated with the surface analysis results presented in this work, by Cerezo et al. [25] and Taheri et al. [26]. For an immersion time of 90 s, the surface of pure zinc and cold rolled steel substrates is completely covered by the Zr-based conversion coating regardless of the hydroxyl fraction. Moreover, the elemental distribution is similar. Therefore, differences in the Open Circuit Potential should be small. On the other hand, for AA6014 important differences in the level of coverage of the film and elemental distribution as a function of the hydroxyl fraction are found. This explains the differences in the potential between specimens with low and high hydroxyl fraction.



Figure 6.10: Potential after 90 s of immersion in the conversion bath for samples with low and high hydroxyl fraction on different metals

6.4. Conclusions

This study is focused, in great part, in assessing the effect of the surface hydroxyls prior the formation of Zr-based conversion films on cold rolled steel. Additionally, the results presented in this study were compared with the ones obtained in our previous studies for AA6014 aluminium alloy and pure zinc. Using ex-situ surface analytical techniques it was proven that under the bath conditions implemented in this study, the hydroxyl fraction does not have a significant effect on the surface chemistry, elemental in-depth distribution and thickness of the resulting conversion layers formed on cold rolled steel. Like in the case of pure zinc, and unlike AA6014, well-defined Zr-based conversion layers were deposited on cold rolled steel for different hydroxyl fractions. This finding is related to the fact that the oxide film on cold rolled steel is unstable in the conversion bath at studied pH. Consequently, the oxide layer is dissolved rapidly giving enough time for the deposition stage to occur.

6.5. References

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7. General conclusions

7.1. Introduction

One of the possible alternatives for the traditional phosphating process as surface treatment for multi-metal surfaces is the Zr-based conversion process. Since most of the cars nowadays are made of different metals one of the main goals of this PhD work was to study and compare the formation mechanism of Zr-based conversion on different metals. Before the Zr-based conversion treatment, a surface conditioning treatment is commonly applied to remove contaminants present at the surface. These treatments can modify the chemistry of the oxide layer of the metal, and therefore the formation of the film can be affected. For that reason, the second goal of the PhD work was to study the influence of the surface chemistry, and more specifically the surface hydroxyls, on the formation of Zr-based conversion coatings on different metals.

7.2. Approach

In this work, a Zr-based conversion treatment based on the immersion of metallic components in a Cu-containing Zr-based conversion solution was evaluated. In the first part of this work, the formation mechanism and surface characteristics of the Zr-based conversion coatings on three different metals was compared. The selected materials in this part of the study were aluminium alloy 6014 (AA6014), cold rolled steel and hot dip galvanized steel. Since the formation of Zr-based conversion films is an electrochemically driven process, the Open Circuit Potential (OCP) was recorded during the immersion of the metals in the conversion bath in order to follow the electrochemical reactions involved in the formation of the film. These measurements were combined with ex-situ surface analysis in order to characterize the resulting films. Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS) and Field Emission AES (FE-AES) were implemented to study the surface chemistry, elemental distribution and thickness of the resulting films. This work was followed by a study on the influence of convection on the deposition of Zr-based conversion coatings on AA6014, cold rolled steel and galvanized steel. For this study, different stirring rates were applied in the conversion bath stirring were studied in-

situ by recording the OCP during the formation of the films. The elemental distribution and thickness of coatings deposited under stirred and stagnant conditions were evaluated by AES depth profiles.

In the second part of this PhD thesis, the influence of the surface hydroxyls on the formation of Zr-based conversion coatings was investigated on AA6014, cold rolled steel and pure zinc. For this part, different model surface conditioning treatments were applied prior to the application of the Zr-based conversion coating in order to promote oxide films with different hydroxyl fractions and similar oxide layer thicknesses. Subsequently, all the surface of the treated specimens were characterized before and after the application of the conversion coatings by means of AES depth profiles, XPS analysis and Field Emission AES. For the different treated metals, the electrochemical reactions during the immersion in the conversion solution were studied by in-situ Open Circuit Potential.

7.3. Formation mechanism of Zr-based conversion coatings on different metals

The results presented in the first part of this work have shown that regardless of the substrate, the formation of the Zr-based conversion coatings follows the same steps. Figure 1 shows a schematic representation of the steps involved in the formation of the Zr-based conversion films. The deposition process starts with the chemical dissolution of the oxide layer by the free fluorides present in the conversion solution. This step is accompanied by the anodic dissolution of the metal. Subsequently, the deposition of the Zr-based conversion layer starts as a result of the alkalinization of the surface promoted by the hydrogen evolution and oxygen reduction reactions. This increase in the pH is accelerated by a preceding deposition of Cu from Cu species present in the conversion bath. The results presented in this work also indicated that the kinetics of each step depend on the metal in which the conversion coating is being formed. In addition, AES-depth profiles revealed that the elemental distribution and thickness of the Zr-based conversion layers are mainly composed by ZrO₂, with small amounts of base metal oxides and fluorides.



Figure 7.1: Schematic representation of the steps involved in the formation of the Zr-based conversion coatings.

On the other hand, it was proven that convection has an important effect on the development and surface characteristics of the Zr-based conversion layer. Open Circuit Potential measurements during immersion in the conversion bath showed several differences in the electrochemical behavior during the formation process as a result of the stirring. AES analysis indicated that for all the studied substrates, thicker films are obtained when the conversion bath is stirred. However, this increase in thickness depends on the substrate. Under the studied conditions, it was found that the film thickness on AA6014 increases about three times when the conversion bath is stirred. For cold rolled steel and hot dip galvanized steel the increase in the film thickness as a result of the conversion bath stirring is approximately two and four times respectively. AES depth profiles also showed that the amount of Cu within the conversion films increases when the conversion solution and chemical dissolution stages in the formation of the conversion coating are accelerated by the mass transport of species as a result of the conversion bath stirring.
7.4. Influence of the surface conditioning treatments on the deposition of Zr-based conversion coatings on different metals

In the second part of this work, it was seen that high hydroxyl fractions on AA6014 are beneficial for the formation of the Zr-based conversion coatings. For samples with hydroxyl fractions between 46 and 52%, the surface is mostly covered by ZrO₂ and only small amounts of aluminium oxide/hydroxides are detected. For specimens with lower hydroxyl fractions, between 13 and 22%, a significant amount of aluminium oxide/hydroxide is detected at the surface after the conversion treatment. In addition, for films formed on samples with high hydroxyl fractions, the resulting film is between two and three times thicker than for low hydroxyl fractions. This behavior was attributed to the first stage in the formation of the Zr-based conversion coatings, which is the chemical dissolution of the oxide layer by the free fluorides present in the conversion bath. The reason of this behavior is that free fluorides mainly interact with the hydroxyl groups, therefore, the chemical dissolution stage occurs more rapidly for samples with higher hydroxyl fractions. As a consequence, more time is available for the deposition stage to take place in the studied time-frame.

On the other hand, FE-AES measurements revealed the presence of Cu-rich zones in Zr-based conversion coatings deposited in differently treated AA6014. FE-AES depth profiles in zones with and without this Cu enrichment indicated that the Zr-based conversion coatings are thicker in these areas. Localized FE-AES spectral analysis of acid and alkaline treated AA6014 have shown a Cu-enrichment at the surface after the surface conditioning treatments. This suggested that the Cu-rich zones observed in the Zr-based conversion films formed on AA6014 can result from the Cu deposition step during the formation of the coatings and also due to localized compositional changes at the surface promoted by the surface conditioning treatments.

This work also has shown that under the studied conditions, the surface hydroxyls have a larger effect on the deposition of Zr-based conversion coatings on AA6014 than on cold rolled steel and pure zinc. For cold rolled steel, it was proven that the resulting hydroxyl fraction does not have a significant effect on the surface chemistry, in-depth elemental distribution and thickness of the Zr-based conversion films. In the case of zinc, well-defined Zr-based conversion films are obtained

regardless the hydroxyl fractions. However, differences in the film thickness are obtained. The reason why the effect of the surface hydroxyls on the deposition of Zr-based conversion films is more pronounced on AA6014 is related to the stability of the oxide films. For the pH of the conversion solution used in this study, the oxide film on AA6014 is stable and therefore the dissolution of stage is highly dependent on the interaction between the surface hydroxyls and the free fluorides present in the conversion bath. This is not the case for cold rolled steel and pure zinc, where the oxide film is unstable at the pH of the conversion bath. All these findings are summarized in Figure 7.2.



Figure 7.2: Effect of the hydroxyl fraction on Zr-based conversion films deposited on different metals.

7.5. Recommendations

Based on the knowledge acquired in this study about the formation of the Zr-based conversion coatings on different metals and the influence of the surface conditioning treatments on this process, further studies can be suggested to have a deeper understanding of this system.

In this work, a Cu-containing Zr-based conversion solution was used to deposit the Zr-based conversion layer. Throughout this study, the composition of the conversion bath was kept constant. Although recently the accelerating effect on the formation of Zr-based conversion films by additions Cu^{2+} ions in the conversion solution [1] was shown, it is scientifically relevant to go deeper into the subject. A possible starting point in this subject would be a study focused on understanding the effect of the Cu^{2+} ions concentration present in the conversion bath in the formation of the Zr-based conversion coatings. This could be done by implementing ex-situ AES depth profiles together with in-situ Open Circuit Potentials to study the in-depth elemental distribution, thickness and kinectics of formation of the conversion film as a function of the Cu concentration in the conversion bath.

To have a better insight on the effect of convection on the formation of Zr-based conversion coatings, Rotating Disk Electrode (RDE) measurements are recommended. These experiments should be combined with ex-situ surface analytical techniques (XPS, AES, etc) to characterize the chemistry and thickness of the conversion films after immersion in the conversion solution at different stirring conditions. Goeminne et al. [2] implemented a similar approach to the one proposed to study the formation of chromate conversion coatings on aluminium.

An important part of this PhD thesis is devoted to understanding the effect of the surface chemistry, and more specifically the hydroxyl fraction on metal oxides, on the formation of the Zr-based conversion coatings. This was done taking into account that with the surface conditioning treatments, the surface chemistry of the oxide films might be modified. However, with the surface conditioning treatments, the oxide layer thickness can also be altered. For that reason, studying the effect of the oxide layer thickness on the deposition of the Zr-based conversion coatings would provide valuable information on the formation mechanism of the films. For this study, it is recommended to form well-defined oxides with similar hydroxyl fractions and different oxide layer thicknesses. In the particular case of aluminium alloys, this can be achieved by applying a barrier layer anodization treatment prior to immersion in the conversion solution. Then, ex-situ surface analysis and in-situ electrochemical analysis can be implemented to assess the influence of this variable on the formation of the conversion layer.

An original and alternative way to investigate in-situ the effect of the oxide layer chemistry and thickness in the formation of the Zr-based conversion coating is by using the Quarz Crystal Microbalance (QCM). This technique was already used by Adhikari et al. [1] to demonstrate the accelerating effect of the addition of Cu species in conversion solution in the formation of the Zr-based conversion layer on different metals. This technique would give direct information about the dissolution stage in the formation of the film. The drawback of this technique is that only pure alloys can be used to follow the formation of the conversion layer. Another way to study this is using in-situ ATR-FTIR during the formation of the Zr-based conversion coatings. This measurements can be combined with in-situ electrochemical techniques [3]. The main disadvantage of this approach is that the metal to be studied has to be deposited on top a crystal. Therefore, the microstructure of the deposited metal will be different than the original substrate. Moreover, some of the treatments implemented in this study, like the thermal treatments, cannot be used because they could damage the crystal.

7.6. References

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Summary

In this PhD work, a new surface treatment based on the application of Zr-based conversion coatings by immersion in a Cu-containing Zr-based conversion solution was investigated as a replacement of the traditional phosphating process for the automotive industry. Nowadays most of the cars are made of a combination of different metals, therefore, one of the aims of this work is to study the formation mechanism of Zr-based conversion coatings on different metallic surfaces. Prior to the immersion in the conversion solution, the metals are exposed to a surface conditioning treatment to remove the contaminants which might interfere in the formation of the film. Taking this into consideration, this PhD thesis is also focused on understanding the effect of the surface conditioning treatments on the deposition mechanism and kinetics of Zr-based conversion coatings on different alloys.

In the first part of this PhD work, the formation mechanism and surface characteristics of Zr-based conversion coatings deposited on aluminium alloy 6014 (AA6014), cold rolled steel and hot dip galvanized steel were evaluated. This was done by combining Open Circuit Potential (OCP) measurements during the formation of the coatings and ex-situ surface analytical techniques. The results indicated that regardless of the metal, the deposition of the Zr-based conversion coating initiates and proceeds by the same mechanism. This process is initiated by the chemical dissolution of the oxide film by the free fluorides present in the conversion bath. This is followed by the deposition of the Zr-based conversion films, which is triggered by the alkalization of the metal/solution interface. Furthermore, the results also showed that the surface chemistry, elemental distribution and thickness of the resulting Zr-based conversion coatings highly depend on the type of metallic substrate. The effect of convection on the formation of Zr-based conversion coatings on different metals was also assessed by implementing in-situ OCP measurements and Auger Electron Spectroscopy (AES) depth profiles. The results indicate that the conversion film thickness increases with the conversion bath stirring rate, but this increment depends on the metal substrate.

The second part of this PhD thesis is focused on understanding the effect of the surface conditioning treatments on the deposition of Zr-based conversion coatings. A surface conditioning treatment can significantly modify the chemistry of the oxide film, such as the fraction of hydroxyl 107

groups present in the outer part of the films. To investigate the influence of this parameter on the formation of the Zr-based conversion films, different model surface conditioning treatments were implemented in order to form oxide films with different hydroxyl fractions at similar oxide layer thicknesses prior to immersion in the conversion solution. The elemental distribution and surface chemistry of differently treated AA6014 and cold rolled steel specimens before and after the formation of the films were evaluated by means of AES depth profiles, Field Emission AES and X-ray Photoelectron Spectroscopy (XPS). The OCP as a function of time was recorded during the formation of the films in order to study the electrochemical reactions involved in the process insitu. The results show that for AA6014, higher hydroxyl fractions are beneficial for the formation of the Zr-based conversion coatings. The observed trend is linked to the effect of surface hydroxyls in the first stage of the formation of the Zr-based conversion coating, which is dissolution of the metal (hydr)oxides by the free fluorides present in the conversion solution. In addition, the results presented in this study indicate an inhomogeneous Cu distribution within the Zr-based conversion layers deposited on the differently treated AA6014. It was concluded that these variations in the Cu composition at the surface originate from the surface conditioning treatment and the Zr-based conversion treatment. The results presented in this part of this PhD thesis show that the largest impact of the surface hydroxyls on the formation of Zr-based conversion coatings is observed on AA6014, followed by zinc and for cold rolled steel no effect was observed.

Samenvatting

Het promotieonderzoek zoals vastgelegd in dit proefschrift richt zich op de toepassing van een nieuwe Zr-gebaseerde oppervlaktebehandeling. Deze conversiecoating, gecreëerd door immersie in een Cu-bevattende hexafluorozirkoonzuur oplossing, werd onderzocht als alternatief voor het traditionele fosfaat-proces in de auto industrie. Tegenwoordig zijn de meeste auto's uit een combinatie van verschillende metalen opgebouwd: één van de doelstellingen was daarom het mechanisme van de formatie van Zr-gebaseerde conversiecoatings op verschillende metaloppervlakken te bestuderen. Voorafgaand aan de formatie van de conversiecoating ondergaan deze metalen een oppervlaktebehandeling waarbij alle verontreinigingen die de formatie van de film kunnen verstoren worden verwijderd. Op basis daarvan is dit proefschrift ook gericht op het onderzoeken van het effect van de oppervlaktebehandeling op het formatiemechanisme en -kinetiek van Zr-gebaseerde conversiecoatings op verschillende legeringen.

Het eerste deel van dit proefschrift behandelt het mechanisme van de formatie en de oppervlakteeigenschappen van Zr-gebaseerde conversiecoatings op aluminiumlegering 6014 (AA6014), koudgewalst staal en thermisch verzinkt staal. Dit werd gedaan door monitoring van de open circuit potentiaal (OCP) tijdens de vorming van de conversiecoating en ex-situ oppervlakteanalyse. De resultaten geven aan dat, ongeacht het type metaal, de formatie van het Zr-laag initieert en verloopt via hetzelfde mechanisme. Dit proces wordt gestart door de chemische oplossing van de oxide-laag door de vrije fluoriden in het conversiebad. Dit wordt gevolgd door de formatie van de Zr-conversiecoating, die geïnitieerd wordt door het alkaliseren van het grensvlak tussen metaal en oplossing. Bovendien toonden de resultaten ook aan dat de oppervlaktechemie, elementaire verdeling en de dikte van de verkregen Zr-conversielaag sterk afhankelijk zijn van het metaalsubstraat. Het effect van convectie op de vorming van Zr-conversielagen op verschillende metalen werd ook bestudeerd door OCP metingen en Auger Electron Spectroscopie (AES) diepteprofielen. De resultaten laten zien dat de dikte van de conversie laag toeneemt bij hogere roersnelheid, maar deze toename hangt af van het metalen substraat. Het tweede deel van dit proefschrift is gericht op de rol van de oppervlaktevoorbehandeling op de formatie van de Zr-gebaseerd conversie coating. Een oppervlaktevoorbehandeling kan namelijk de chemie van de oxidelaag sterk beïnvloeden waaronder ook de hydroxyl-fractie in het buitenste deel van de laag. Om de invloed van deze parameter op de vorming van de Zr-conversielaag te onderzoeken zijn verschillende oppervlaktevoorbehandelingen uitgevoerd om oxides met verschillende hydroxylfracties en een vergelijkbare dikte te vormen. Verschillend voorbehandelde AA6014 en koud gewalst stalen proefstukken werden dan vóór en na de laagvorming geëvalueerd door middel van AES diepteprofielen, Field Emission AES en X-Ray photoelectron spectroscopie (XPS). Tijdens de vorming van de laag werd ook de OCP gevolgd als functie van de tijd, met het doel om de elektrochemische reacties in-situ te bestuderen. De resultaten toonden aan dat een hogere initiële hydroxyl-fractie gunstig is voor de formatie van Zr-conversiecoatings op AA6014. Deze waargenomen trend is gekoppeld aan het effect van oppervlakte-hydroxylgroepen gedurende de eerste fase van de formatie van de Zr-gebaseerde conversielaag, namelijk het oplossen van de metaal(hydr)oxiden door de vrije fluoriden in het conversiebad. Bovendien, de gevonden resultaten in deze studie lieten een inhomogene verdeling van Cu in de Zr-gebaseerde conversiecoatings zien op de verschillend voorbehandelde AA6014 substraten. Er kan worden geconcludeerd dat deze variaties in de Cu samenstelling aan het oppervlak worden geïnitieerd door zowel de oppervlaktevoorbehandeling als de Zr-gebaseerde conversiebehandeling. De resultaten geven het grootste effect van oppervlakte-hydroxylgroepen aan op de formatie van Zr-gebaseerde conversiecoatings op AA6014, gevolgd door zink en koudgewalst staal waar geen effect wordt waargenomen.



Appendix: Complementary figures

Figure a1: AES depth profiles for the a) alkaline treated and b) reference sample.



Figure a2: AES depth profiles of the Zr based conversion coating deposited on the a) acid b)alkaline treated and c) reference sample.

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