Growth Kinetics and Structure of Zr4/Cr3 Based Conversion Coating over Aluminium

Kalaivanan Thirupathi1*, Pál Bárczy2 and Gabor Lassu3

1Institute of Ceramics and Polymer Engineering, University of Miskolc, Miskolc, Hungary.
2Matmod Ltd., Miskolc, Hungary.
3Institute of Metallurgy, University of Miskolc, Miskolc, Hungary.
*Corresponding author

ABSTRACT

In this study, the structure of Zr4/Cr3 based conversion coating on aluminium alloys was studied by using the Glow Discharge – Optical Emission Spectroscopy (GD-OES) method. Samples were examined before and after exposure to high vacuum. The results revealed that the structure of the coating has two different phases, solute and gelatinous state. The growth kinetics of conversion coating is investigated by considering the thickness of the coating under various immersion times inside the coating bath. The present data suggest that coating growth kinetics has five different states, namely activation, linear growth, limited growth, saturation limit and detachment state. The conversion coating structure over aluminium alloys such as AA2024 and AA6082 was investigated in detail to understand the influence of the substrate in coating formation. The results imply that the formation mechanism strongly depends on alloying elements of the substrate. Conversion layer growth involves dissolution and deposition of ions. It was found that the alloying elements have a slowdown influence on aluminium dissolution. The results imply that high alloyed aluminium tends to form a coating with less thickness and lower Zr-Cr concentration.

I. INTRODUCTION

Conversion coating is widely used for the protection of aluminium alloys [1]. The recent prohibition of hexavalent chromate conversion coating due to its toxic and hazardous nature has led to more intense research to find a replacement [2]. Zr4/Cr3 based conversion coating seems to be the best alternative treatment [3]. The developments published related to this conversion coating show successful results in corrosion protection behaviour over aluminium alloys and provides good adhesion over paints [4].

The coating bath consists of trivalent chromium and zirconium salts [5]. Studies of the formation and layer structure of the coating using several techniques over AA2024 alloy reveal that the coating forms in a double layer. XPS (X-ray photoelectron spectroscopy) spectrum analysis shows that the coating has an inner aluminium-rich layer containing a mixture of oxygen and fluoride species while the outer layer consists of zirconium and chromium species [6]. It has been reported that conversion coating exhibits a similar formation mechanism over three alloys, namely AA2024, AA7075 and AA6061 [3].

Published investigations about coating thickness measurement mentioned under vacuum coating undergoes severe dehydration [7]. Here, we use high vacuum as a tool to predict the structure of coating and reveal the elemental changes that occur during exposure to high vacuum. Besides, the study on coating growth kinetics over pure aluminium alloy using AFM (Atomic Force Microscope) and TEM (Transmission Electron Microscope) indicated that coating growth has three states: an active period up to 30 s, a linear state lasting to 600 s and changes to limited growth after 1200 s [8]. The study was done on pure aluminium; thus, the influence of alloying elements is not well defined. To discover this, we have coated AA6082 alloy sample under various immersion time to predict growth kinetics of conversion coating inside bath.

An investigation about formation of coating over AA2024 reveals that the coating has several cracks and detachment over substrate. The coating over enriched copper-rich particles shows some change in formation, as mentioned in [9]. This indicates that alloy elements have a major
contribution in the formation of the coating [10]. However, not many studies have been carried out previously to understand the influence of the substrate in the formation of Zr4/Cr3 conversion coating. In the present study, we analyse this knowledge gap using GD-OES, the most sensitive depth profile technique [11]. One goal of this paper is to understand the effect of high vacuum on the coating structure and thickness. Further, we also investigate the formation mechanism of coating and the influence of two different substrates.

II. EXPERIMENTAL PHASE

A. Specimen and Preparation

Metal samples with the composition as given in Table 1 were obtained as 15×15 mm sheets 4 mm thick. The specimens were initially cleaned with detergent and rinsed with isopropyl alcohol, ethanol and acetone for few seconds. The surface of samples was modified by mechanical polishing to 800 grid finishes and then was electro polished using Struers electrolyte A2 I and II (50% v/v) at 20 V for 60 s around 25 °C followed by rinsing using DI water, ethanol and drying in a cool air stream. The degreased samples were etched with 5 Vol% of NaOH for 180 s and desmutted with H2SO4 solution of 17 v/v % for 180 s. Both pre-treatments were carried out at room temperature. The samples were thoroughly rinsed using deionised water after each pre-treatment. All of the oxide free alloy samples from both alloys were treated at various immersion times such as 60, 300, 600, 1440, 1920, 2280 s at 40 °C using a SurTec 650 bath with pH 3.8 followed by deionised water rinsing. After the coating procedure all samples were dried at room temperature for 24 h before depth profiling to predict the influence of alloying elements. In addition, we used high vacuum effect as tool to predict coating structure. Some samples were exposed to 10-7 mbar vacuum in a chamber for two hours before depth profile investigation to evaluate any differences in coating by comparing exposed and non-exposed samples.

Table 1 Elemental composition of alloy (wt. %).

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Si</th>
<th>Cu</th>
<th>Mg</th>
<th>Mn</th>
<th>Cr</th>
<th>Ti</th>
<th>Zn</th>
<th>Ni</th>
<th>V</th>
<th>Ga</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA 6082-T651</td>
<td>0.20</td>
<td>1.100</td>
<td>0.053</td>
<td>0.99</td>
<td>0.7</td>
<td>0.028</td>
<td>0.011</td>
<td>0.062</td>
<td>0.004</td>
<td>0.012</td>
<td>0.009</td>
<td>97%</td>
</tr>
<tr>
<td>AA 2024-T351</td>
<td>0.19</td>
<td>0.008</td>
<td>4.2</td>
<td>1.5</td>
<td>0.52</td>
<td>0.01</td>
<td>0.060</td>
<td>0.03</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>93%</td>
</tr>
</tbody>
</table>

B. Glow Discharge Optical Emission Spectroscopy (GD-OES)

GD-OES is one of the most sophisticated techniques for the analysis of thin film owing to its unique combination of fast sputtering rate, high depth resolution, excellent sensitivity and multi-element capability [12]. In this technique, cathodic sputtering is used to remove each layer from the surface of sample. The glow discharge source is filled with argon gas under low pressure (0.5 to 10 hPa). The atoms removed from the surface undergo inelastic collision; the electrons transfer their kinetic energy to argon atoms, which causes them to dissociate into argon cations and further electron, this mixture is called plasma [13]. The characteristics spectrum emitted by the excited atoms is measured by a spectrometer. The intensity is recorded as a function of time. Based on the sputtering depth on the measured sample, measured using a surface profilometer, the sputtering time is transformed to a quantitative content depth profile.

The elemental analysis was done by a GD-profile instrument with copper anode of 4 mm diameter using a flushing time of 30 s, a pre-integration time of 30 s, background of 5 s, pressure of 635 Pa, power of 35, a module of 7.2 and a phase of 4 V. The emission lines used for this analysis were 396.157 nm for Al, 324.759 nm for Cu, 383.834 nm for Mg, 339.230 nm for Zr, 452.439 nm for Cr, 589.600 nm for Na and 130.223 nm for O. The obtained results were analysed neglecting the effects of contamination, surface roughness or variation in sputtering rate of each element. Therefore, the initial 10-20 nm in each examination is neglected from the GD-OES graph, as shown in Figure 1. All numerical values that represent coating thickness have been consider with ± 20 nm.

III. RESULTS AND DISCUSSION

A. GD-OES Curve

Figure 1 shows an elemental analysis of the coating over AA6082 alloy for 600 s immersion time. The first peak in graph indicates the point where the sputtering of coating begins, and the second peak represents the interface between the coating and substrate. Here the thickness of the coating was considered as the distance between the two peaks. It is obvious that our interpretation is approximate, since after the second peak around 300 nm there is a decreasing tendency for Zr, Cr and O curves with a slight increase in alloying elements such as Mg, Cu curves. In this regard, we assume a transient zone caused by the measurement accuracy limitations. So we can conclude that the coating thickness of this sample is around 300 nm.

The legend indicates the list of elements used for coating analysis with GD-OES. The ions that do not show any significant variation before the second peak are considered to be unavailable in the coating region. The intensity value on the Y axis is an arbitrary unit which does not represent the exact element composition of coating. Instead of that, shapes of curves are analyzed to detect changes in coating composition. Both the Zr and Cr curve exhibited similar shapes. Because of the minor Cr content in substrates, Zr distribution curves are considered exclusively for coating thickness measurements.
Figure 1 Typical GD-OES atomic distribution in coated AA6082 alloy.

B. Formation Mechanism

Figure 2 shows distribution of ions in that coating that formed over AA6082 alloy coated for 300 s. O, Cr and Zr curves have high intensity up to 3 s, after which the intensity gradually drops, whereas the aluminium curve has less intensity for the first few seconds, after which it climbs very high. It is also significant from this graph that other alloying elements are not present in the coating region. Interestingly, the same coating over another sample that is exposed to high vacuum (Figure 3) reveals a slight drop in Cr, O and Al curves with complete disappearance of the Zr in the coating. Comparing Figure 2 and Figure 3 the disappearance of the second peak is probably result of tremendous shrinkage in the coating after vacuum exposure [14].

Figure 2 Coating over AA6082 (sol-gel).

We interpret this phenomenon by assuming that the coating has two different phases. The first is the Al-Cr-O phase in gel form. The second phase is in the form of a low viscosity solute that mostly consists of Zr ions with smaller amounts of Cr3 and Al ions. This second phase can be removed from the coating by exposure to high vacuum. Based on these results, we predict the formation mechanism of coating inside the conversion bath.

Figure 3 Coating over AA6082 alloy after vacuum exposure (gel).

Both ions inside the coating bath and those dissolved from the substrate are involved in coating formation. The change in temperature and pH causes aluminium from the metal to dissolve into Al3+ ions, as shown in Figure 4. This is because Al3+ ions are stable in an aqueous solution, as known from the aluminium Pourbaix diagram [15]. The Zr4+ and Cr3+ ions already existing within the coating bath react with aluminium ions, converting the surface of aluminium alloys into a complex mixture of all three ions in various forms such as oxides, hydroxide, sulphates, and fluorides [6]. The layering kinetics starts near the surface of the aluminium by formation of a molecular chain of a complex mixture of Zr4 and Cr3 components. The Zr4 is mostly kept its solute state throughout the conversion process, and it is assumed to be surrounded by hydroxide with cluster-like behaviour. Interestingly, some of the Al filters through the molecular oxide chain film and is dissipated into sol phase. In summary, the conversion coating formed over aluminium alloys has a two-phase sol-gel structure that is observed by exposure to vacuum.

Figure 4 Formation of coating over two alloys.

C. Coating Growth Cycle

The growth cycle of conversion coating was investigated by measuring the thickness of the
coating as a function of immersion time. Figure 5 shows five Zr distribution curves indicating that the coating reaches a maximum thickness of 450 nm around 1440 s, after which there is a tremendous change in curve shape. The coating growth process has obviously ceased. The experimental results are summarized in Table 2, representing the various coating thicknesses as a function of immersion time.

![Zr curve](image)

**Figure 5** Zr distribution in sample coatings formed over AA6082 removed from coating bath after different immersion times.

**Table 2** Thickness of coating formed over AA6082 alloy under various immersion times.

<table>
<thead>
<tr>
<th>State</th>
<th>Time s</th>
<th>Coating thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation</td>
<td>0-60</td>
<td>0 - 100</td>
</tr>
<tr>
<td>Linear</td>
<td>60-540</td>
<td>~100 -310</td>
</tr>
<tr>
<td>Limited</td>
<td>540-900</td>
<td>~310-400</td>
</tr>
<tr>
<td>Saturation</td>
<td>900-1440</td>
<td>~450</td>
</tr>
<tr>
<td>Detachment</td>
<td>Above 1440</td>
<td>~55</td>
</tr>
</tbody>
</table>

Based on these data, we propose a coating growth model consisting of five different states. The Figure 6 represents the growth cycle of Zr4/Cr3 conversion coating over AA6082 alloy.

The coating growth consists of five different states: activation, linear growth, limited growth, saturation and detachment states.

- The activation state is the initial period when the aluminium starts its dissolution and the conversion process begins. The coating reaches maximum 100 nm during this state. This state starts when the samples is immersed in to coating bath below 60 s.
- The linear growth state is the period where the formation of the coating is more rapid. The aluminium dissolution inside the coating bath is abundant and rapid conversion occurs over the surface of the alloy. Almost the entire surface of the substrate is covered in a long molecular chain network of Cr, Zr, Al and O ions.
- In the limited growth state aluminium dissolution is disturbed by the coating that had previously formed over substrate. This reduces further formation of the coating because there are not many Al ions that can pass through molecular network to react with Cr3 and Zr4 ion in the coating bath. We assume that aluminium somehow dissolves in certain region such as cracks, which tends to contribute to coating growth. The growth of the coating is very slow during this state compared to the previous two states.

![Coating growth cycle](image)

**Figure 6** Coating growth cycle.

- The saturation limit is the point where there are no more dissolution ions from the substrate. The coating reaches its maximum limit, beyond which there is no more coating growth. This saturation limit varies according to the size of the sample and its composition. Most of the samples reached this limit at approximately 450 nm. The saturation limit can occur at different times and coating thicknesses over one sample. We conclude that for AA6082 sample with thickness ~450 nm has a saturation limit around 1440 s, after which the next state begins.
- The detachment state is the point where the coating is detached from substrate and disappears in the coating bath. We believe that after the saturation limit the coating cracks in several places and a large agglomerate of Cr, Zr and Al ions in the coating dispatches from the surface of the alloy. However, the chemistry behind this dispatch is unknown. The coating thickness measured beyond this detachment state represents the regrowth of coating.
D. Effects of alloying elements during the conversion process

Figure 7 shows the distribution of aluminium and zirconium in coatings over A6082 and AA2024 alloys after 300 s immersion bath for 300 s. The graph indicates that under the same immersion time aluminium dissolution is less and the layer is thinner with less zirconium for AA2024 compared to AA6082. Since AA2024 is high alloyed by copper ions, we predict that disturbs the dissolution rate of Al ions. In case of AA6082 the dissolution rate is high, which is the root cause for thicker coating growth over various immersion times. Over all, the dissolution process is dependent on the standard reduction potential of ions, as is evident from the literature [16]. The Si (-1.7) and Al (-1.6) has higher values in comparison to Cu (+0.15). The Si ions give priority for dissolution of aluminium more inside solution compared to Cu ions. This causes the variation in coating thickness formation over two alloys, as shown in Table 3.

Table 3 Coating thickness variation (nm) for two different alloys.

<table>
<thead>
<tr>
<th></th>
<th>0 s</th>
<th>60 s</th>
<th>300 s</th>
<th>600 s</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA2024</td>
<td>0</td>
<td>36</td>
<td>180</td>
<td>114</td>
</tr>
<tr>
<td>AA6082</td>
<td>0</td>
<td>90</td>
<td>110</td>
<td>258</td>
</tr>
</tbody>
</table>

Table 3 indicates the variation in thickness of coating of AA6082 and AA2024 alloy with increase in immersion time. It is evident that the thickness of the coating increases with immersion time. From these results, our hypothesis is that layer formation seems to be highly dependent on the quantity of alloying elements in the substrate over which the coating is formed. The aluminium dissolution determines coating thickness.

IV. CONCLUSION

In conversion coating on AA6082 aluminium alloy sol and gel states were found to be separable in high vacuum. The sol part mostly consists of Zr and small amount of Cr, Al and O, whereas the gel phase constitutes large molecule structures of Cr-Al-O.

The kinetics of coating growth is classified in five different states that is activation, linear growth, limited growth, saturation limit and dispatch state. The time duration of these stages may be various depending upon substrate and its alloys.

The formation mechanism of Zr4/Cr3 coating is highly dependent on the alloying elements of the substrate. The dissolution of aluminium in the coating bath determines the formation of coating and growth.

V. ACKNOWLEDGEMENTS

The authors would like to thank Tamás Bárczy and Béla Somosvári Márton at Admatis Ltd, Hungary for their valuable contribution to experiments. This project was financed by ESA under Environment Friendly Conversion Coating Development (ECD) to MATMOD Ltd, Contract: No. 4000114580/15/NL/ND.

VI. REFERENCES


