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Effects of Vacuum and Ageing on Zr4/Cr3 based Conversion Coatings on Aluminium Alloys

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In this study, we investigate the impact of ageing and high vacuum on existing environmentally friendly Zr4/Cr3-based conversion coatings. The freshly formed coating undergoes several changes during ageing and exposure to high vacuum. Based on the present data, we propose that the coating formed over AA6082 and AA7075 alloys is sol-gel in nature, confirmed by secondary neutral mass spectroscopy (SNMS) using the depth profiling technique. Our findings reveal that there are elemental level changes that result in shrinkage of the coating. Most Zr ions in the coating are in the solute form, with lesser number of Cr and Al ions that disappear under high vacuum over a certain period of time. The remaining Cr, Zr and O atoms exist in a gelatinous state. During ageing, there is a continuous transition of ions from solute to gelatinous state. In addition, the deposition of coating ions is directly influenced by the substrates and their constituents. The extent of dissolution of aluminium in the conversion bath determines both Zr and Cr ion deposition. For a highly alloyed metal like AA7075, the dissolution rate is disturbed by copper and zinc.

Keywords - Zr4/Cr3 based conversion coating, SNMS, sol-gel structure.

I. INTRODUCTION

Aluminium alloys such as AA6082 and AA7075 are widely used in aircraft and space metallic components due to their light weight and favourable mechanical properties. It is necessary to protect the metal surface with a coating that provides good resistance against corrosion and good adhesion to the top coat [1]. Hexavalent chromium-based conversion coating is widely used for aluminium alloys. However, its toxic, hazardous and carcinogenic nature has led to an urgent need to find eco-friendly replacements, as mandated by various directives of the European Union [2].

Among potential alternative treatments, Zr4/Cr3 based conversion coating has shown promise. [3]. This conversion bath usually consists of zirconium fluorides and trivalent chromium salts [4]. The formation mechanism of conversion coating over AA2024 alloy has been studied for several years, and it is now known that this process involves dissolution and redeposition of ions from the substrate as well as the chromium bath, with interfacial pH variation during the coating [5][6]. Investigations on the growth of coating over AA2024 indicate that this coating consists of two layers, an outer layer containing a greater number of Zr and Cr species and an inner layer rich in oxides and fluorides of aluminium [7][8]. In one study, the impacts of ageing using AA2024 alloy as a substrate were studied and it was suggested that the coating becomes more hydrophobic at elevated temperatures [9]. While there are

studies on the formation of coating over AA7075, research on the effects of high vacuum and ageing related to Zr4/Cr3 based conversion coating over AA6082 and AA7075 alloys is limited. The structure of this coating has not been studied or reported so far. A TEM (Transmission Electron Microscope) image of coating over AA2024 shows that the coating is porous in nature [10]. However, not much is known about the impact of vacuum or influence of sample preparation. In particular, the effect of alloying elements in the substrate has not been investigated in previous research related to conversion coating. However, the coating formed over AA2024 revealed several cracks and detachments over the copper enriched area. This suggests that alloying elements may significantly contribute to the formation of coating [11].

In the present study, we analyse differences in the formation mechanism of coatings over the AA6082 and AA7075 alloys using the SNMS depth profiling technique. The aim of these experiments is to understand the impact of ageing and high vacuum.

II. EXPERIMENTAL PHASE

A. Specimen preparation

The elemental composition of the alloy samples was determined by inductively coupled plasma optical emission spectrometry (ICP-OES), summarized in Table 1. Samples were obtained as 10×10 mm sheets of 4 mm thickness [12]. The received specimens were initially cleaned with detergent and rinsed with isopropyl alcohol, ethanol and acetone for a few seconds. The surfaces of the samples were first modified by mechanical polishing up to 800 grid finishes, and were then electro polished using Struers electrolyte A2- I and II (50 v/v %) at 20 V for 60 s at approximately 25 °C. This was followed by rinsing with deionised water and ethanol, and then drying in cool air stream. Polished AA6082 samples were etched in 5 v/v % of NaOH for 180 s and desmutted with H₂SO₄ solution (17 v/v %) for 180 s. Both pre-treatments were carried out at room temperature. The AA7075 samples were pre-treated as follows: (i) etching in NaOH at 5 v/v % for 180 s at 60 °C (ii) desmutting using 50 v/v % H₂SO₄ for 180 s at room temperature. All samples were thoroughly rinsed using deionised water after every step.

All the oxide-free alloy samples were treated for 180 s at 40 °C using a SurTec 650 bath with elemental composition as mentioned in datasheet [13] at a pH of 3.8, followed by rinsing with deionised water. After rinsing, samples that were

investigated after 24 h of coating were labelled as “fresh”, while those analysed after three weeks of ageing in laboratory conditions at room temperature were labelled as “aged”. Some

of the fresh samples were placed in high vacuum (10^{-7} mbar) for 2 hours.

| Elements (Wt. %) | Zn | V | Ti | Sn | Si | Pb | Ni | Mn | Mg | Ga | Fe | Cu | Cr | Bi | Al |
|------------------|-------|-------|-------|-------|------|--------|--------|-------|------|-------|-------|-------|-------|-------|------|
| AA6082-T651 | 0.014 | 0.012 | 0.012 | 0.007 | 1.09 | 0.003 | 0.005 | 0.71 | 0.99 | 0.008 | 0.237 | 0.092 | 0.008 | 0.002 | 96.7 |
| AA7075-T651 | 5.87 | 0.009 | 0.036 | 0.002 | 0.07 | 0.0019 | 0.0045 | 0.011 | 2.55 | 0.014 | 0.009 | 1.85 | 0.192 | 0.005 | 89.3 |

Table 1: Elemental composition of the investigated alloys (wt. %)

B. Secondary Neutral Mass Spectroscopy (SNMS)

Elemental depth profile analysis of coatings on various substrates was performed using an INA-X type SNMS system (SPECS GmbH Berlin) at ATOMKI in Debrecen, Hungary. SNMS is a unique thin-film analysis method utilizing post-ionization. The post-ionization medium increases the probability of ionization of neutral particles sputtered from the sample surface. The INA-X device uses electron cyclotron wave resonance (ECWR) plasma as an ion source for both sputtering and post-ionization with sputtering energies of a few 100 eV. The system is equipped with a quadrupole type mass spectrometer up to 340 AMU for detecting elements. Basically, samples were bombarded and post-ionized using an inductively coupled low pressure radio frequency Ar discharge. The Ar ions were extracted from the plasma to sputter the sample surface with a high frequency negative bias on the sample. Residual ions were then identified by energy dispersive ion optics. The bombarding energy of Ar ions over the coated sample was around 350eV with a plasma pressure of 1.5 mbar. The elemental composition of the coating was determined using sensitivity factors of the constituents. The sputtering time was converted to depth by calibrating the sputtering rates with a profilometer. During profiling, sputtering yield changes due to layer density change were also taken into account [14]. The depth scale was fixed by accepting the nominal surface roughness of the sample before and after measurements [15]. Almost all ions from the conversion coating bath and substrate were somehow involved in layer formation. From experimental data, we concluded that oxygen, aluminium, chromium, and zirconium were the main building elements of the layer, since the peaks of other alloying elements such as zinc, magnesium, silicon, iron, copper, and manganese were not observed.

III. RESULTS AND DISCUSSION

A. SNMS Curves

A typical layer structure of a coated AA6082 alloy is shown in Fig. 1. The intensity was measured in CPS (counts per second), indicating the relative number of detected atoms. As seen in Fig. 1, the oxygen content tends to decrease, but it is retained inside the layer. The aluminium curve indicates a different behaviour. On the surface, its value is minimum, but after leaving the layer, a sharp increase is observed up to up to a maximum, with no further change beyond a depth of 200 nm. The zirconium and chromium curves show elongated peaks at 30–80 nm depths, with a slow transient toward

increasing depths. We interpret these curves up to their peaks to represent the coating area, whereas the deeper part of the curve is believed to be a phantom segment caused due to surface roughness. The SNMS figures also confirm the absence of a sharp transition between the substrate and coating. We interpret that the $\sim 0.34 \mu\text{m}$ surface roughness of the coated samples decreases depth resolution, thus elongating interfacial regions in the curves.

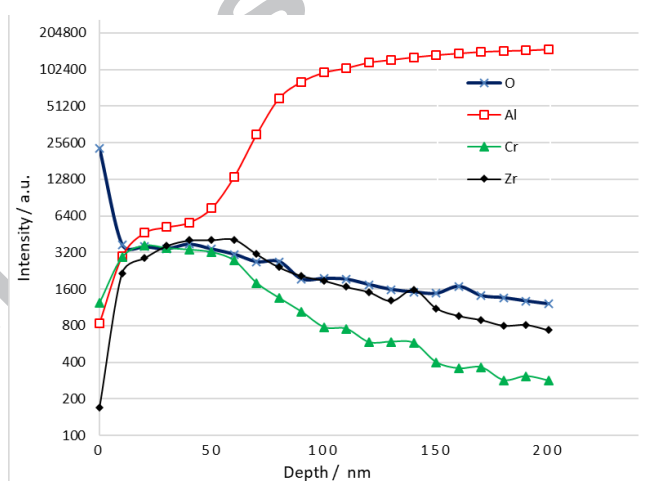


Fig. 1- Typical SNMS atomic distribution in a coated AA6082 alloy.

B. Effects of high vacuum on coating structure

Fig. 2 presents the concentration distributions of Al, Cr, Zr and O ions as a function of sputtering time at fresh state over an AA6082 sample. It can be seen that the Cr and Zr curves have peaks, whereas the O and Al curves show monotonous decreasing or increasing trends. The concentration distribution for another AA6082 sample analysed after high vacuum treatment is shown in Fig. 3. Comparing these figures, the O curve does not significantly change, but the Al and Cr curves radically decrease after high vacuum exposure. Interestingly, Zr ions completely disappear from the layer. In addition, layer shrinkage is also apparent after comparing both figures.

To interpret these phenomena, we assume that the coating has a two-phase structure. The first phase is the -Al-O-Cr-molecular chain, building a gel-like network. The second is a low- viscosity sol phase, composed of mostly Zr with a few Cr ions from the coating bath and some Al ions from the substrate. This second phase proved to be removable from the network under high vacuum. The layering process seems to follow interesting kinetics. Electron interchange toward Cr ions begins with Al ions near the surface of the substrate,

leading to molecular chain growth. Some Al ions from the solute can travel through the filtering network and dissipate in the sol phase. The nature of this sol phase is not fully understood. We assume that the Zr ions are surrounded by hydroxides in a cluster-like behaviour, in which some of the Cr and Al ions are in sol state. In summary, the conversion coating has a two-phase sol-gel structure that is observed after exposure to vacuum. A similar sol-gel effect has been observed from the depth profiling using glow discharge optical emission spectroscopy (GD-OES) of coated samples that were exposed to high vacuum [16].

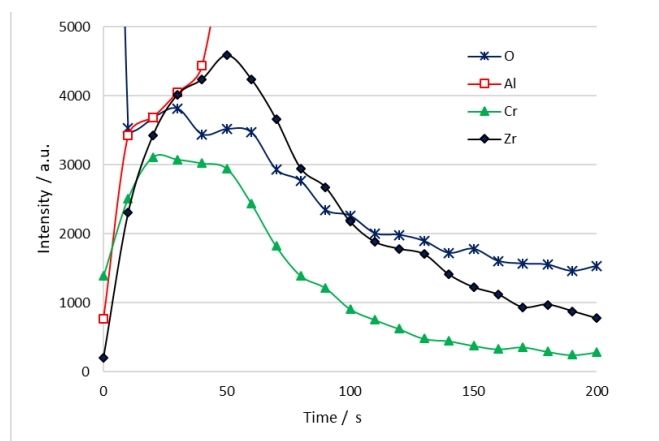


Fig. 2- Atomic distribution in a coated AA6082 prior to vacuum exposure (sol-gel structure).

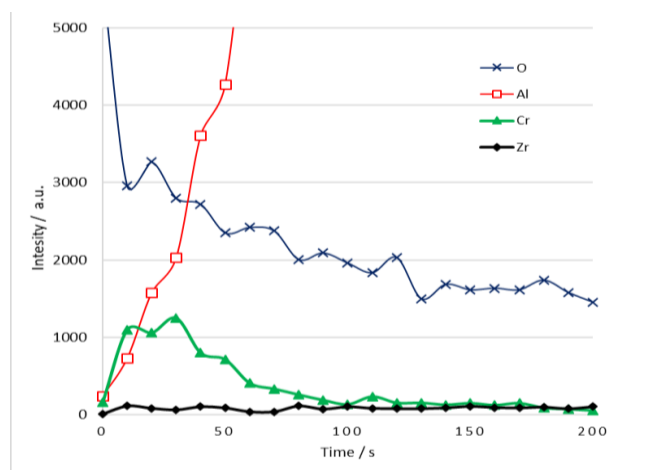


Fig. 3- Atomic distribution in a coated AA6082 after high vacuum treatment (gel structure).

C. Influence of alloying elements and ageing

To study the effects of alloying elements during the conversion process, a series of coated samples were examined by SNMS under the same experimental parameters. Fig. 5, including both aged and fresh samples, indicates that the intensity of Zr and Cr ions over AA6082 alloy is much higher than that over AA7075. Interestingly, in all the graphs the intensity of Cr is higher for the first few nanometres of coating depth, followed by a higher intensity of Zr ions. Furthermore,

the Cr and Zr ion peaks extend until 100 nm for AA6082, while their intensity is lowered after 40 nm in the AA7075 curves. The fresh coated AA6082 samples seemed to have higher aluminium content inside the coating than that in the AA7075 samples, as seen in Fig. 4. This implies that the formation mechanism is highly dependent on the quantities of alloying elements in the substrate over which the coating is being formed. The alloying elements in the substrate also play a vital role in coating growth. We interpret this phenomenon to suggest that coating formation mainly depends on the dissolution of aluminium ions inside the conversion coating bath. In the case of AA7075, dissolution is disturbed by alloying elements such as copper and zinc. The dissolution process is controlled by atomic standard potential values. Mg (-2.7) and Al (-1.6) have higher values compared to those of Zn (-0.76) and Cu (+0.15) [17]. Therefore, Al and Mg ions are prioritized, whereas the dissolution of Zn is delayed, and Cu ions do not dissolve. This disturbance results in reduced ion exchange for the formation of Zr and Cr in the coating, as presented in Fig. 5 (a,c). In addition, the SNMS figures do not show any sharp transition curves between coating and substrate, thereby validating that the coating so formed is a homogenous mixture. This makes the determination of coating thickness using SNMS difficult as compared to other surface analytical methods. The chemistry of the coating surface with dependence of alloying elements will be analysed in our next paper using GD-OES [16].

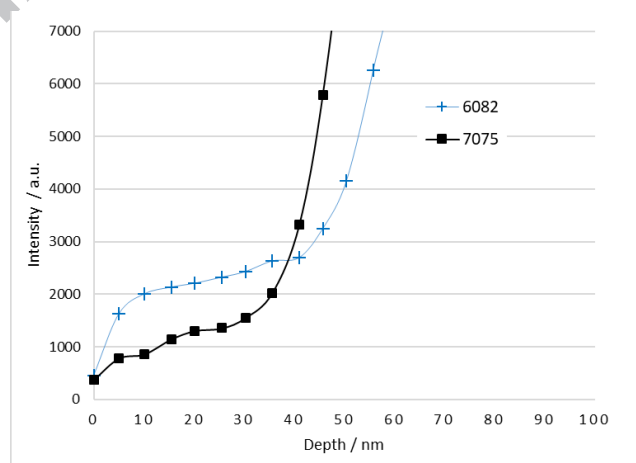


Fig. 4- Al distribution in fresh AA6082 and AA7075 coated samples.

The effect of ageing has not been studied in detail in this study, but literature indicates that ageing plays a major role in conversion coating behaviour. The ageing process means drying the coating for a certain period of time to achieve the proper structure. We studied the ageing effect using SNMS to discover structural transformation. The fresh and aged SNMS curves show that the oxygen curve is drastically reduced inside the coating for the AA7075 alloy during the ageing process, as seen in Fig. 5 (c,d). This finding signifies that there are some changes at an elemental level during the ageing process. In addition, other curves like Zr and Cr do not undergo any major change. In the fresh state, the coating formed over AA7075 has

a higher oxygen curve compared to that of AA6082. We assume that the sol-gel proportion is a probable reason for this variation. It is also observed from Fig. 5 (a and b) that the aluminium content of the AA6082 alloy is slightly reduced after ageing. From this SNMS analysis of fresh and aged samples, we predict that there is a change in the chemical state of the coating. A previous report suggests the coating undergoes dehydration in the ageing process. Our hypothesis is that once the samples are taken out of the bath, the coating

undergoes a continuous transition from solute to gelatinous state. Based on the results of the high vacuum exposure, we found that mostly Zr ions are in sol form, with some Al and Cr ions. In summary, atoms in the coating tend to change their nature from solute to gelatinous states during the ageing process. This sol-gel transformation at room temperature appears to take a surprisingly long time (weeks or months), most probably caused by the slow Zr clusters.

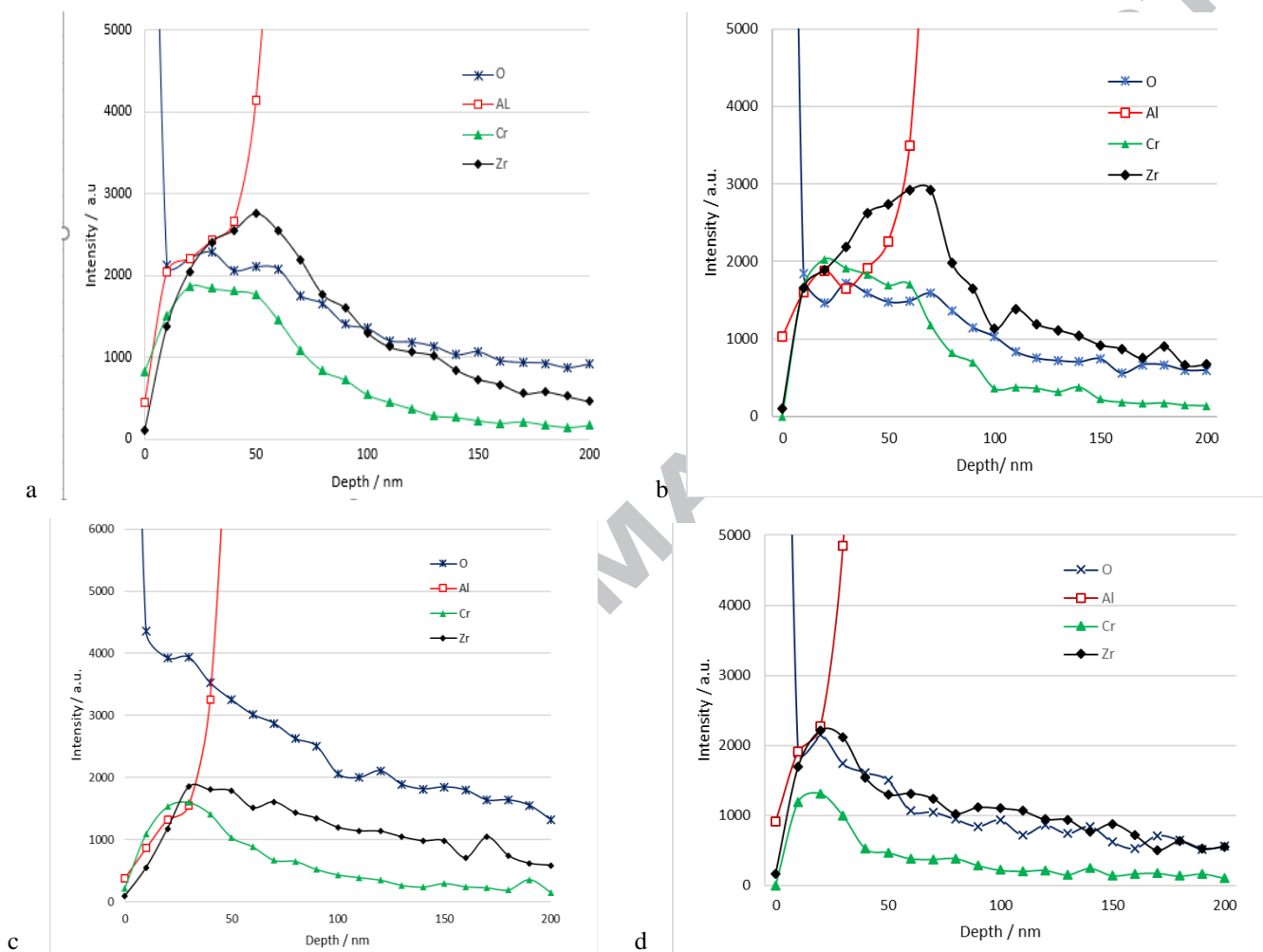


Fig. 5- Atomic distribution in fresh (graphs a,c) and aged (graphs b,d) coatings formed over AA6082 and AA7075.

IV. CONCLUSIONS

Ageing and vacuum effects

- Based on the SNMS measurements, we have found that the Zr₄/Cr₃ based conversion coating exhibits a sol-gel type structure.
- The disappearance of Zr ions from the fresh coating under high vacuum can be interpreted as a sol-gel process, with Zr ions dominating in the sol and Cr-O-Al molecule chains predominating in the gel.
- The reduction in oxygen and variation in aluminium intensity under ageing indicates that the coating undergoes a continuous change from sol to gel.

Substrate influence

- The Zr₄/Cr₃ conversion coating is based on dissolution of aluminium into the bath and ion exchange. This process is decelerated and halted by the alloying elements in the substrate, resulting in a thin layer with a low chromium content.

V. ACKNOWLEDGEMENTS

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High lights for review

In literature, this coating is mentioned as trivalent chromium conversion coating but we have named it as Zr⁴/Cr³ based conversion coating because both atoms contribute in formation of coating.

- The Sol- Gel structure for Zr⁴/Cr³ conversion coating over aluminium alloys based on results from SNMS,
- The disappearance of Zr ion in high vacuum for coating
- The elemental level changes that occur in coating during aging
- The influences of alloying elemental in substrates over which Zr⁴/Cr³ coating is formed

Grammar was modified in this revised paper