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Accelerated growth of oxide film on aluminium alloys under steam: Part I: Effects of alloy chemistry and steam vapour pressure on microstructure

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ABSTRACT

Aluminium alloys were treated with steam of varying vapour pressures which resulted in the growth of aluminium oxyhydroxide layers of an average thickness of ~450–825 nm. The microstructure and composition of the generated layers were characterised by GD-OES, FEG-SEM, GI-XRD and TEM. The thickness of the oxide layer as well as the compactness increased with steam vapour pressure. The increase in vapour pressure also resulted in a better coverage over the intermetallic particles. Oxide layer showed a layered structure with more compact layer at the Al interface and a nano-scale needle like structure at the top. The kinetics of formation of film under steam was rapid; approx. 350 nm thick layers were generated within 5 s of steam treatment, however increase in thickness of the oxide retarded further growth. The enrichment or depletion of different alloying elements at the surface of aluminium as a result of alkaline etching pre-treatment influenced the thickness and growth of the oxide. Moreover the steam treatment resulted in the partial oxidation of second phase intermetallic particles present in the aluminium alloy microstructure.

1. Introduction

Aluminium alloys are becoming increasingly attractive today due to the possibility of translating their light weight coupled with high strength into a number of applications, mainly in the automotive industry in order to meet the growing demands for more fuel-efficient vehicles by reducing energy consumption and environmental pollution challenges [1]. Corrosion resistance is an important aspect in all these applications for aluminium alloys. As the protection provided by the native oxide layer on aluminium is not good enough for long term protection against corrosion, additional surface treatments are needed. Conversion coatings are commonly used to protect aluminium alloys against various types of corrosion phenomenon [2] and for improved adhesive properties [3]. Over the last few decades anticorrosive chromium based conversion coatings were extensively used on aluminium alloys [4–6]. However due to the carcinogenic nature of hexavalent chrome, alternatives of chromate based conversion coatings are in pursuit. The main approach to find alternatives for chromate conversion coatings, involve rare earth based inhibitors, anodising and sol–gel coatings [5,7]. In the aluminium industry, Ti/Zr [8], phosphate and permanganate [9] based conversion coatings are being used as a substitute for chrome based conversion coatings.

The thin native oxide film on aluminium surface is of great interest for corrosion protection due to its interesting dielectric properties. The native oxide film can be hydrated (to form boehmite or pseudo-boehmite) at elevated temperatures by reaction with water [10]. The growth of hydrated aluminium oxyhydroxide on aluminium by immersion in boiling water was extensively studied from the 1960s to 1970s [11,12]. Alwitt and Hart [10,13] reported on the formation of bayerite in the temperature range of 40–60 °C for long exposure of aluminium in water and observed that nucleation of bayerite decreased with increase in temperature. Draley et al. [14] reported that only boehmite was present after immersion of aluminium in water after 30 days above 60 °C. Our earlier studies [15] have shown the formation of more than 500 nm thick boehmite films by the use of high temperature and pressurised steam. The formed oxide was reported to have a nano-scale needle like structure that is uniformly distributed on the aluminium surface and exhibited a high corrosion resistance. The presence of hydroxyl groups on the outer surface of the oxide film produced on aluminium under hydrothermal conditions has also been reported [16,17]. Hydroxyl groups are beneficial for increasing the adhesion of polymer coatings and adhesives to the surface treated aluminium alloys [18,19]. Therefore, it is expected that a thickened boehmite coating will possess the necessary properties for corrosion resistance as well as to provide good adhesion to the applied top paint layers. However, a detailed study of the effect of high temperature steam on oxide growth on aluminium and underlying mechanisms has not been reported in the literature.

In the present work (Part I), the effect of pressurised steam at different vapour pressures generated inside an autoclave on the oxide growth on aluminium alloys (AA1090 and Peraluman 706™) has been investigated in detail. Microstructure, surface morphology, oxide growth mechanism, composition of the oxide layer and phase analysis were

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investigated as a function of steam parameters using GD-OES, FEG-SEM, TEM, EDS, and GI-XRD. Part II of this paper describes in detail the investigation of the corrosion performance including filiform corrosion performance and adhesion of a powder coating.

2. Experimental

2.1. Materials

Aluminium alloys AA1090 and Peraluman 706™ were used as substrates for all the investigations. The alloys were obtained in the form of cold rolled sheet with thickness of 0.5 mm and 1 mm respectively. All the samples were cut from the sheet into 50 mm × 50 mm coupons. Table 1 shows the composition of the alloys determined by GD-OES analysis. The difference in the composition at near surface of the used aluminium alloys when compared to the standard composition can be due to cold rolling process and use of lubricant in the cold rolling process [20,21].

2.2. Surface preparation

2.2.1. Treatment 1

Only degreasing treatment is carried out for individual samples by immersion in 6 wt.% commercial Alficlean™ (pH = 9) aqueous solution for 2 min at 60 °C followed by rinsing in deionised water for 1 min and air drying at room temperature.

2.2.2. Treatment 2

Samples were subjected to alkaline etching treatment by immersing in an aqueous solution of 10 wt.% NaOH at 60 °C for 5 min, rinsing in deionised water for 1 min followed by desmutting in 69 vol.% HNO_3 for 2 min. The samples were then rinsed with deionised water and dried in air at room temperature.

2.3. Steam treatment

Specimens pre-treated using treatment 1 and treatment 2 were subjected to pressurised steam treatment in an autoclave. The surfaces of the specimens were exposed to 5 psi, 10 psi, and 15 psi (gauge pressure) pressurised steam which was generated from deionised water in an autoclave (All American Pressure Canners, USA). The total process time was 25 min, while the time of exposure after the autoclave reached steady state conditions was 10 min. The maximum temperature measured by Thermax (TMC, UK) surface indicator strips, at 5 psi (1.3 bar), 10 psi (1.6 bar), and 15 psi (1.9 bar) internal pressure in the autoclave was 107 °C, 113 °C, and 118 °C respectively. The vapour pressure of the steam was calculated in bar using Antoine equation [22].

$$\ln P^\circ = -B/T + C + A$$

where P is vapour pressure, B, C, and A are the component specific constants for Antoine equation and T is the temperature at which the vapours are generated.

Table 1
Composition at the surface of material (wt.%, balance Al).

Alloy	Fe	Si	Mn	Mg	Cu
AA1090	0.4 ± 0.05	1.2 ± 0.08	2.7 ± 0.1	0.1 ± 0.02	0.08 ± 0.01
Peraluman 706™	0.6 ± 0.07	0.4 ± 0.05	0.8 ± 0.09	1.5 ± 0.04	0.13 ± 0.03

2.4. Surface characterization

2.4.1. Compositional depth profiling

Compositional depth profiling across the thickness of the steam treated surface was carried out using glow discharge optical emission spectroscopy (GD-OES) (GD-2 profiler, Horiba Jobin YVON). The instrument is equipped with a radio frequency generator, a standard discharge source with an anode of 4 mm internal diameter, a monochromator and polychromator optical spectrometers and Quantum XP software. The optimised discharge conditions for this work were 850 Pa pressure and RF power 40 W.

2.4.2. Surface morphology

The morphology of the aluminium alloy surfaces before and after the steam treatment was investigated using a field emission gun scanning electron microscope (FEG-SEM-Quanta 200 FEG MKII, FEI) with an Oxford Instrument INCA EDS analyser capability. The EDS analysis has been performed with an acceleration voltage of 10 keV and Cu calibration.

2.4.3. Transmission electron microscopy

Thin film lamella from the steam treated surfaces were prepared using in-situ focussed ion beam (FIB-SEM) lift out (Model Quanta 200 3D DualBeam, FEI) and were further thinned for electron transparency in a FIB-SEM (Helios Nanolab DualBeam, FEI). Transmission electron microscopy was carried out on the prepared lamella using a transmission electron microscope (TEM) (Model Tecnai G2 20) operating at 200 keV. The EDS compositional analysis was performed in S-TEM operational mode.

2.4.4. Grazing incidence X-ray diffraction (GI-XRD)

Phase analysis of the oxide layers generated on the aluminium samples was performed using a diffractometer (D8 Discover, Bruker AXS) equipped with a Cu Kα X-ray source. The XRD measurements were performed at a grazing incidence angle of 2°, a step time of 40 s, and step size of 0.03°.

3. Results

3.1. Glow discharge optical emission spectroscopy (GD-OES)

Fig. 1 shows a typical GD-OES depth profile of Peraluman 706™ sample after steam treatment for 10 min. The concentration of elements shown by the GD-OES profile can be relatively compared; a decrease

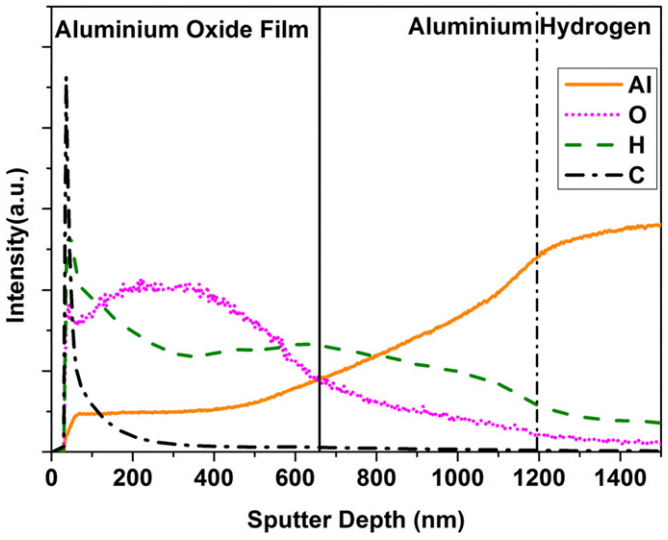

Fig. 1. GD-OES depth sputter profile of Peraluman 706™ after exposure to pressurised steam of vapour pressure 1.3 bar for 10 min.