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Steam Assisted Accelerated Growth of Oxide Layer on Aluminium Alloys

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Summary

Corrosion resistance of aluminium alloys is related to the composition and morphology of the oxide film on the surface of aluminium. In this paper we investigated the use of steam on the surface modification of aluminium to produce boehmite films. The study reveals a detailed investigation of the effect of vapour pressure, structure of intermetallic particles and thickness of boehmite films on the corrosion behaviour of aluminium alloys.

1   Introduction

Aluminium and its alloys are widely used in structural and transportation industry owing to their high strength to weight ratio [1]. The surface of aluminium under normal conditions has a thin oxide film (2.5-10 nm) responsible for its inherent corrosion resistance. This oxide film can further be converted or transformed into functional conversion coatings in order to enhance durability and adhesion to paint systems [2]. Chromium based conversion coatings have been extensively used on aluminium alloys to improve adhesion of subsequent paint layers and corrosion resistance. However, the use of hexavalent chromium is strictly regulated due to its toxic nature and suspected carcinogenicity [3]. So, it is highly imperative to develop other alternatives for chrome conversion coatings. Treatment of aluminium with natural water at elevated temperatures results in the formation of different forms of aluminium oxide (γ-AlO(OH) , Al(OH)$_3$) depending on the preparation parameters/conditions [5]. Moreover, with the knowledge of factors controlling film growth, composition and morphology, such oxide layers carry huge potential for practical applications. This study highlights the effect of steam vapour pressure on the oxide growth on aluminium alloys. The growth and composition of the oxide layer was investigated in detail as a function of microstructure using GD-OES, SEM, EDS, XRD and XPS. Potentiodynamic polarization measurements were used to study corrosion behaviour of the produced boehmite films.

2   Experimental

2.1   Materials

Aluminium alloys AA1090 (99.94 wt. %) and Peraluman 706™ (99.7 wt. %) aluminium sheet with the thickness of 0.5 mm and 1mm respectively were used. All samples were cut from the sheet into 50 mm x 50 mm coupons.

2.2 Surface preparation

2.1.1 Treatment 1

Individual samples were degreased in a 6 wt. % commercial Alficlean aqueous solution at 60 °C for 2 min followed by rinsing in distilled water and air drying.

2.1.2 Treatment 2

Individual samples were immersed in an aqueous solution of 10 wt. % NaOH at 60 °C for 5 min, rinsed in distilled water, followed by desmutting in 69 vol. % HNO_3 for 2 min. They were then washed with distilled water and dried in air.

2.3 Steam Treatment

Following the above surface treatment processes, the specimens were exposed to 5 psi, 10 psi, and 15 psi pressurized steam generated from deionized water in an autoclave (All American Pressure Canners, USA). The steam treatment was carried out for approx. 10 min after a steady state condition was achieved within 25 min time. The maximum temperature measured by Thermax (TMC,UK) surface indicator strips, at 5 psi,10 psi, and15 psi internal pressure in an autoclave was 107 °C, 113 °C, and 118 °C respectively. The vapour pressure of steam was calculated by using Antoine equation.

$$\ln P° = -B/T + C + A \qquad [4]$$

Where P is vapour pressure, B, C and A are the tabulated values of water for Antoine equation. T is the temperature at which vapours are generated.

2.4. Characterization

The morphology of the aluminium surfaces before and after the steam treatment was studied in field emission scanning electron microscope (FEG-SEM-Quanta 200F, FEI) equipped with an Oxford Instrument INCA EDS analyser.

Depth profiling compositional analysis of steam treated samples were carried out with glow discharge optical emission GD-2 profiler instrument manufactured by Horiba Jobin YVON.

The XPS analysis were performed using Thermo scientific X-ray photo electron spectrometer with a monochromatic Al X-ray source at 1486 eV with dual beam source for charge compensation. Each analysis started with a survey scan from 0 to 1100 eV. The base pressure was approximately 2.0E-8 mbar. The binding energies were referenced to C1s line at 284.4 eV from the adventitious carbon. For all samples XPS survey spectra and high resolution spectra (O1s and Al2p) were obtained.

Phase identification of the generated oxide layer on the AA1090 aluminium samples was characterized using XRD (D8 Discover, Bruker AXS) with Cu Kα radiation at a grazing incidence angle of 2°, a step time of 40 s, and step size of 0.03°.

Potentiodynamic polarization measurements were carried out using an ACM Instruments (GillAC). A cell set-up with an exposed area of 0.95 cm^2 was used for measurements. The open circuit potential (OCP) was maintained for 5 min before the polarization was started. Anodic and cathodic sweeps were conducted in naturally aerated 0.1 M NaCl solution. Ag/AgCl electrode was used as reference and Pt was used as counter electrode. The scan rate of measurements was 1 mV/s starting from a potential close to OCP.

3   Results and discussion

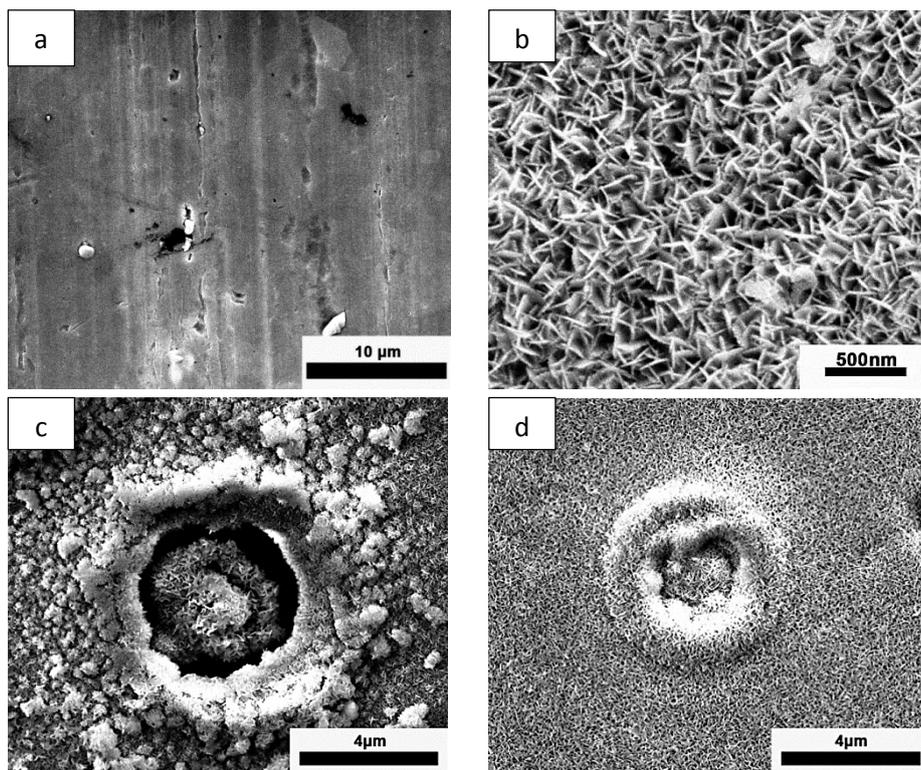### 3.1   Surface Morphology of formed oxide layer

Figure 1: Scanning electron micrographs of aluminium surface after treatment with pressurised steam for 10 mints with 1.3 bar water vapour pressure

The surface morphology of Peraluman 706 after 10 min steam treatment using pressurised steam generated in an autoclave operating under a vapour pressure of 1.3 , 1.6, and 1.9 bar at 107°C, 113°C, and 118°C respectively, produced a needle type structure (Figure 1b). It was observed that due to difference in water vapour pressure, the morphology of the oxide films changed in terms of porosity. Films produced at high vapour pressure were denser than at lower water vapour pressure of steam after 10 min of steam treatment. The same phenomenon was observed on AA1090 surface. Short time exposure of the sample to pressurised steam (5 s for all above mentioned water vapour pressures) resulted in the formation of a thin oxide film on aluminium surface. This film was transformed into platelet like crystals which serve as nucleation sites for further transformation. The transformation proceeds by growth and coalescence of these platelets into needles. The transformation process is very fast and takes place within the first 5 s of the steam treatment thus covering

most of the sample area. The growth of oxide over the intermetallic particles contained in the aluminium matrix was however not homogenous.

The surface defects in the aluminium matrix and intermetallic particles were covered with an oxide of a different kind of morphology, which can be best described as a "cauliflower". The size of these structures was in the range of 1 – 25 µm. Further, some of these structures also appear to be surrounding a hole in the aluminium matrix (Figure 1c, Figure 1d). The extent of oxide growth over intermetallic particles was mainly dependent on vapour pressure. In this study, the mechanism of oxide film growth from the reaction between aluminium and water can be divided into three basic steps as follows: (i) formation of amorphous oxide, (ii) dissolution of the amorphous oxide, and (iii) precipitation of the dissolved species as hydrous oxide [5][6]. The needle like features appearing in the outer surface layers of aluminium oxide (Figure 1b) were due to the evolution of hydrogen gas which diffuses through the oxygen defects present in the amorphous oxide layer and produces nucleation sites for boehmite. A similar feature has been observed earlier by several researchers [7] [8].

3.2   Glow discharge optical emission spectroscopy

Radio frequency GD-OES has recently been demonstrated to be an extremely powerful and reliable technique for compositional depth profiling analysis of thin, insulating barrier oxide films formed on aluminium surfaces [9]. Figure 2 shows thickness of oxide films formed on aluminium surface measured with GD-OES analysis at different vapour pressure of steam after 10 min of treatment.
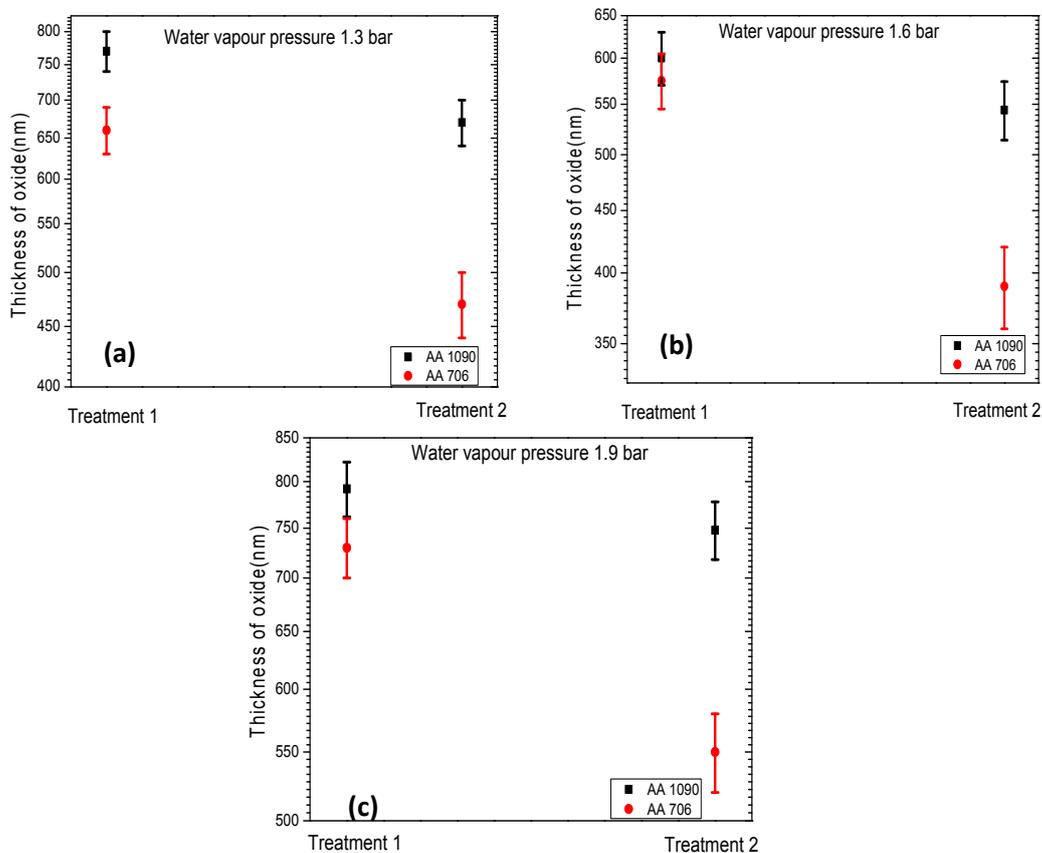

Figure 2 Growth of oxide on AA1090 and Peraluman 706 after treatment 1, 2 at different exposure time of pressurised steam with water vapour pressure of: (a) 1.3bar (b) 1.6 bar (c) 1.9 bar respectively.

Figure 2a shows that the thickness of oxide was higher on AA1090 than on Peraluman 706 after treatment process 1. After treatment process 2, the thickness of oxide decreased on both the substrates. The thickness of the oxide was higher on AA1090 because of the presence of fewer intermetallic phases than those in Peraluman 706. After treatment process 2, the thickness of the oxide decreased on both the aluminium substrates due to higher population density of second phase particles as compared to the alloy surface (treatment process 1). These second phase particles influence the dissolution rates of the alloys [10].

3.3 Corrosion behaviour

Figure 3a shows potentiodynamic cathodic polarization curves of Peraluman 706 samples after steam treatment for 10 min with pressurised steam at different vapour pressure. Significant decrease in the cathodic activity was observed for steam treated samples as compared to reference aluminium. The steam treatment at different vapour pressures has lowered the cathodic activity by a factor of 100 which is indicated by the shift of cathodic curves to lower current density values. Anodic activity Figure 3b decreases with steam treatment of samples. The samples treated at 1.9 bar water vapour pressure show the lowest anodic activity. This is expected to be due to the formation of thick barrier layer as compared to steam treated samples with 1.3 and 1.6 bar water vapour. It also shows that the oxide layer formed by steam vapour pressure of 1.3 and 1.6 bar starts to fail above a potential level (-500 mV for 1.3 bar and -250 mV for 1.6 bar), but the oxide layer formed with a steam vapour pressure of 1.9 bar was stable even at higher potential levels.
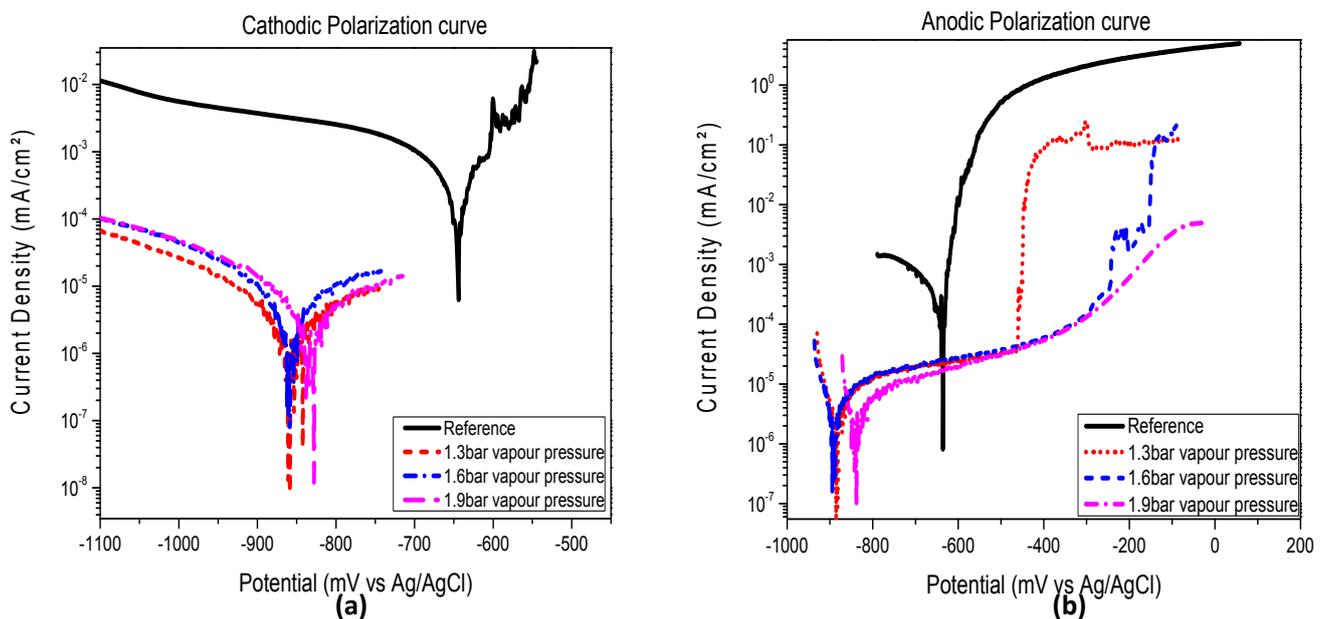

Figure 3(a) Cathodic polarization curves **(b)** Anodic polarization curves of Peraluman 706 (treatment process 1) before and after exposure to the pressurized steam of different water vapour pressure for 10 min.

3.4 X-ray photoelectron spectroscopy (XPS)

Figure 4 shows the O1s spectrum from the steam treated AA1090 sample surface. The presence of three different oxygen species is visible from the spectrum. In addition to the bulk oxygen with a binding energy of 531.7 eV from the crystal

structure, the surface of oxide contains hydroxyl groups with an O1s binding energy of 530.4 eV and amount of adsorbed water with an O1s binding energy of 533.4 eV which is in agreement with the boehmite O1s mineral spectra [11] [12] [13].
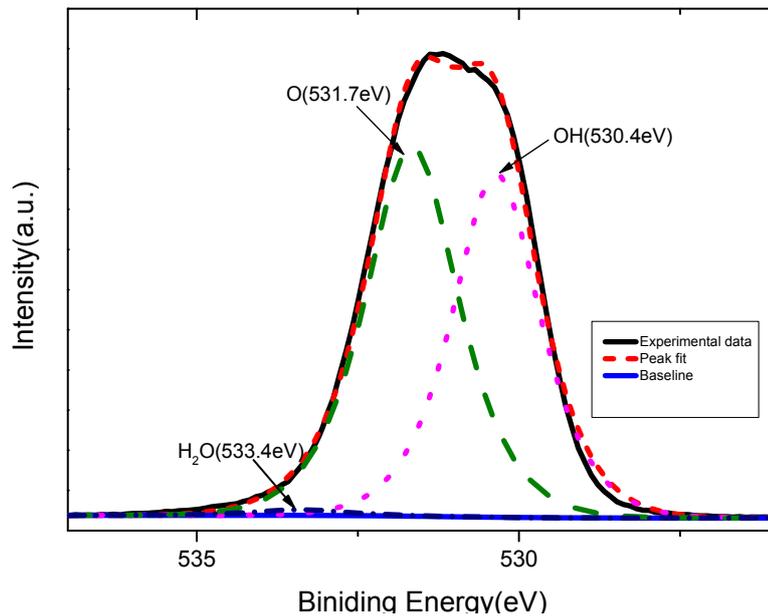

Figure 4 O1s spectra on the surface of AA1090 after 10 min of steam treatment with a water vapour pressure of 1.6 bars.
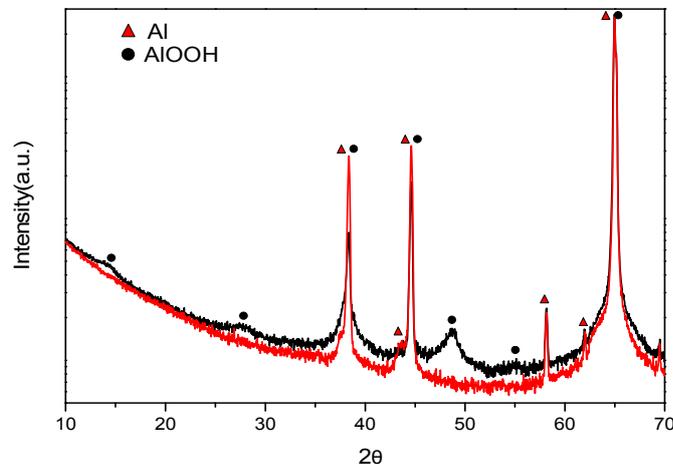
3.5 XRD

Figure 5 X-ray diffractogram of AA1090 after 10 min of steam treatment with water vapour pressure of 1.3 bar.

Four main X-ray diffraction peaks at 2θ = 14.4, 27.2, 49 and 55° corresponding to AlOOH phase can be seen in the sample after treatment which were not revealed in the pure Al. The result shows that the oxide formed on the surface of aluminium was γ-AlOOH.

Overall the results show the possibility of accelerated growth of oxide film on aluminium alloys using steam. Further work is on the way and will be the focus of a more detailed journal paper.

4   Conclusion

Highly pressurised steam at different vapour pressure produces aluminium hydroxides (boehmite) of different porosity and thickness depending on the water vapour pressure. The boehmite film of ~350 nm can be generated on aluminium surface within 30 s of surface treatment of aluminium with steam. Partial dissolution or dislodging of intermetallic particles is also a function of vapour pressure of steam. The generated oxide film at different vapour pressure of steam reduces the cathodic activities 100 times due to the formation of barrier layer and dislodged/dissolved intermetallic particles. The surface preparation methods also have a significant effect on the growth of boehmite films. The average thickness of generated boehmite films after 10 min of steam treatment was in the range of 500-850 nm, which can serve as an intermediate coating on aluminium for various purposes.

Acknowledgements:

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