

## **EFFECTS OF ANODIZING PORE STRUCTURE ON THE ADHESIVE BONDING PERFORMANCE OF AA5754 AUTOMOTIVE SHEETS**

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### **ABSTRACT**

Three types of anodic films (unsealed, hot water sealed and agent sealed) were prepared to study the effects of anodizing pores structure on the adhesive bonding performance of AA5754 automotive sheets. The morphology of the anodic films was examined by using scanning electron microscope (SEM) and the composition was examined by glow discharge optical emission spectroscopy (GDOES). The adhesive bonding strength and durability in corrosive environment were investigated by using single lap shear test and salt spray corrosion test (SST), respectively. The results showed that the pores structure could significantly influence the adhesive bonding performance. The unsealed sample showed porous structure and provided high bonding strength, however, the durability was poor in corrosive environment. The hot water sealed sample showed fine and loose hydrated alumina structure on the surface and provided high durability in corrosive environment, but the bonding strength was low. In contrast, the agent sealed sample provided both high bonding strength and durability in corrosive environment.

### **KEYWORDS**

Aluminum alloy, Anodizing, Glow discharge optical emission spectroscopy (GDOES), Lap-shear, Corrosion

## INTRODUCTION

Adhesively bonded aluminum joints by using adhesives have been widely used for the realization of lightweight design in industrial applications like automotive and aerospace industry [1, 2]. Durable bonds which are capable of taking structural loads can be created due to a careful consideration of the way in which the joint is formed, the type of adhesive and the appropriate treatment of the adherend surfaces prior to bonding [3-6]. Experiences demonstrate that the surface treatment is the most critical step which could not be disregarded, since it is essential to achieve long-term service capability [7]. In structural applications, a bonded assembly is expected to maintain a significant load and may be combined with exposure to harsh environmental conditions in its service life. For this purpose, the pretreatment for structural bonding of aluminum alloy must provide not only strong tensile strength and durability but also good corrosion resistance. Chromic acid anodizing (CAA) process provides an anodized layer which has good corrosion resistance while also exhibiting useful adhesion characteristics as well as lacquer coating retaining characteristics [8]. However, the use of Cr (VI) is unadvised from a health and environmental point of view since it is toxic and carcinogenic, and this process is gradually limited even prohibited. Boeing's phosphoric acid anodizing (PAA) process provides a more open pore structure allowing penetration of high molecular primers/adhesives [8] and PAA process is the most widely used pre-surface treatment suitable for adhesive bonding between aluminum alloy components. Rahimi et al. demonstrated that nanostructure can be produced by PAA process and is affected by the time of pretreatment and anodizing parameters [9]. Xu et al. investigated the influence of surface energy and roughness on adhesive bonding through PAA process and provided improved adhesion performance under certain anodizing parameter [10]. However, PAA process is normally not recommended for a major concern of deterioration of the mechanical performance of the joints as a result of exposure to a wet and corrosive environment. Sulfuric acid anodizing (SAA) process, recently, has been widely used for corrosion protection and good base coating for the adhesion of lacquers in aerospace manufacturing [11]. The good performance is explained by properties such as the porous morphology and high adsorptive power of the oxide film, the chemical and electrical inertness of the anodized layer. Moreover, modified sulfuric acid could also be used for adhesive bonding. Lunder et al. found that anodizing in hot sulfuric acid is promising as a simple, very rapid and environmentally friendly pre-treatment for adhesive bonding [12]. Saeedikhani et al. studied the process of phosphoric/boric/sulfuric acids anodizing and found it was a promising pre-treatment for adhesive bonding of aluminum alloys instead of the chromic acid anodizing process [13]. However, the corrosion resistance is also rather limited because the porous anodic layer could be easily penetrated by corrosive ions. The traditional environmental hot water sealing process could provide certain corrosion resistance but would destroy the porous structure. That would lead to the decrease of bond strength, and thus is not widely accepted for structure bonding in practice [14].

In this study, a simple SAA process, which is composed of anodizing and sealing procedure, is introduced for corrosion protection and adhesive bonding. A porous anodic layer suitable for bonding is obtained by anodizing process, and the following sealing procedure improves the corrosion resistance. The presence of sealing agent could help maintain the porous morphology of the anodic film. The corrosion resistance of the anodized aluminum alloy was evaluated by electrochemical impedance spectroscopy (EIS) and the bonding strength was measured through single lap shear test.

## EXPERIMENTAL

Aluminum 5754 alloy plates (major elements, wt.%: Mg 2.0–4.0, Si 0.05–0.2, Fe 0.2–0.4, Cu 0.05–0.1, Mn 0.1–0.4) were cut in size of 125×80×2 mm for anodizing and lap-shear testing. Prior to anodizing, the samples were degreased and alkaline etched in 90 g/L sodium hydroxide electrolyte at 68°C and then de-smutted in 200 g/L nitric acid electrolyte at room temperature. Anodizing was carried out in 180 g/L sulfuric acid electrolyte for 15 min with applied current density of 1.4 A/dm<sup>2</sup>. The electrolyte was vigorously stirred to maintain the temperature at 18°C. Each step was followed by thoroughly rinsed in distilled water.

After anodizing, three samples were prepared:

- (1) The unsealed sample was just anodized and rinsed without any further treatments.
- (2) The hot water sealed sample was anodized and immersed in de-ionized water for a period of 20 min at 98°C.
- (3) The agent sealed sample was anodized and immersed in de-ionized water with the addition of 3 g/L sealing agent for a period of 20 min at 98°C.

Afterward, all samples were dried in an air circulating heating cabinet.

Field Emission Scanning Electron Microscopy (FE-SEM) was applied to examine the topography of aluminum alloy after anodizing treatment. Glow discharge optical emission spectroscopy (GDOES) combines sputtering and atomic emission was used for element depth profiling. Sensitivity of GDOES method is at the ppm level due to the relatively large area analyzed in this case 4 mm in diameter.

Single lap-shear testing was performed by using a commercial epoxy based structural adhesive, Betamate 4600F, with joints of 20 mm overlap to evaluate the bonding strength. Configuration of the samples are shown in Figure 1. The thickness of adhesive was controlled by using glass beads to the value of 0.2 mm. Curing was performed for 30 min at 180°C in an air circulation furnace with metallic clips used to keep the two coupons together. Afterward, the testing was carried out with a universal testing machine MTS Model C64, where five samples were tested in each case.

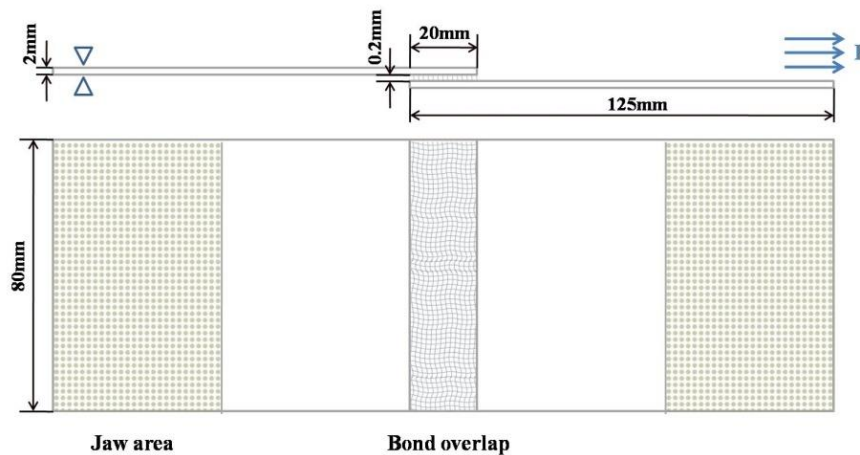


Figure 1. Shapes and dimension of bonding samples

## RESULTS AND DISCUSSION

The anodizing process provides uniform and flat anodic layer on the surface of substrate alloy and a porous morphology was observed (Figure 2a). The porous film is composed of hexagonal cells with pore size of approximately 2–20 nm in diameter. The hot water sealing procedure modifies the surface of anodic layer through hydration reaction, developing a fine and loosen morphology and the porous layer was totally covered (Figure 2b). In contrast, the agent sealed sample shows the similar porous structure as the unsealed sample (Figure 2c). Presence of sealing agent seemly prevents the formation of hydration compounds on the surface, however, it was still unclear whether the inner pores were effectively sealed.

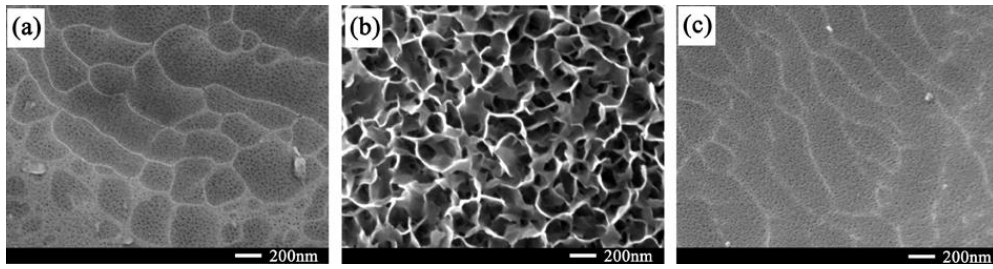
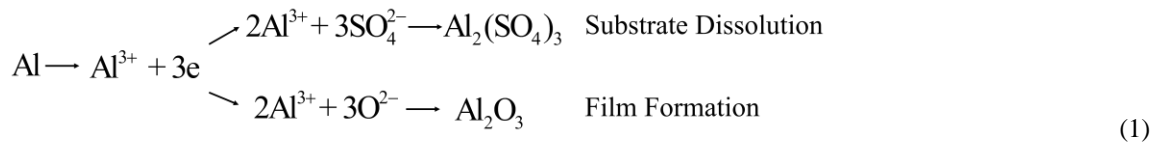


Figure 2. Surface morphology of anodized 5754 aluminum alloys: (a) Unsealed, (b) Hot water sealed, (c) Agent sealed

The diameter of the pores was so small that it was difficult to observe the microstructure of the nanopores in the length wise direction. Quantitative GDOES depth profiles provided sufficient composition information along the anodic layer, and the pore structure could be also deduced. The anodic oxide layer covered samples (unsealed, hot water sealed and agent sealed) displayed similar curve shape, and we used the unsealed sample as a representation (Figure 3a). It is observed that the concentration of Al element gradually increases while O element decreases with the increase of sputter depth as determined from spectrographic analysis. Meanwhile, Mg element gradually increases from almost 0 to a constant concentration of 3.5%, which is in good agreement with the alloy composition. Presence of S element is expected to be associated with  $Al_2(SO_4)_3$  that formed during sulfuric acid anodizing process. A peak value of S element is observed locating at the depth position of  $\sim 6\mu m$ . This agrees well with the thickness of anodic oxide film. During anodizing, the formation of anodic film could be depicted as follows:



these two reactions occurred right at the interface between anodic film and the substrate alloy. Consequently, location of the peak value of S element was associated with the thickness of anodic film.

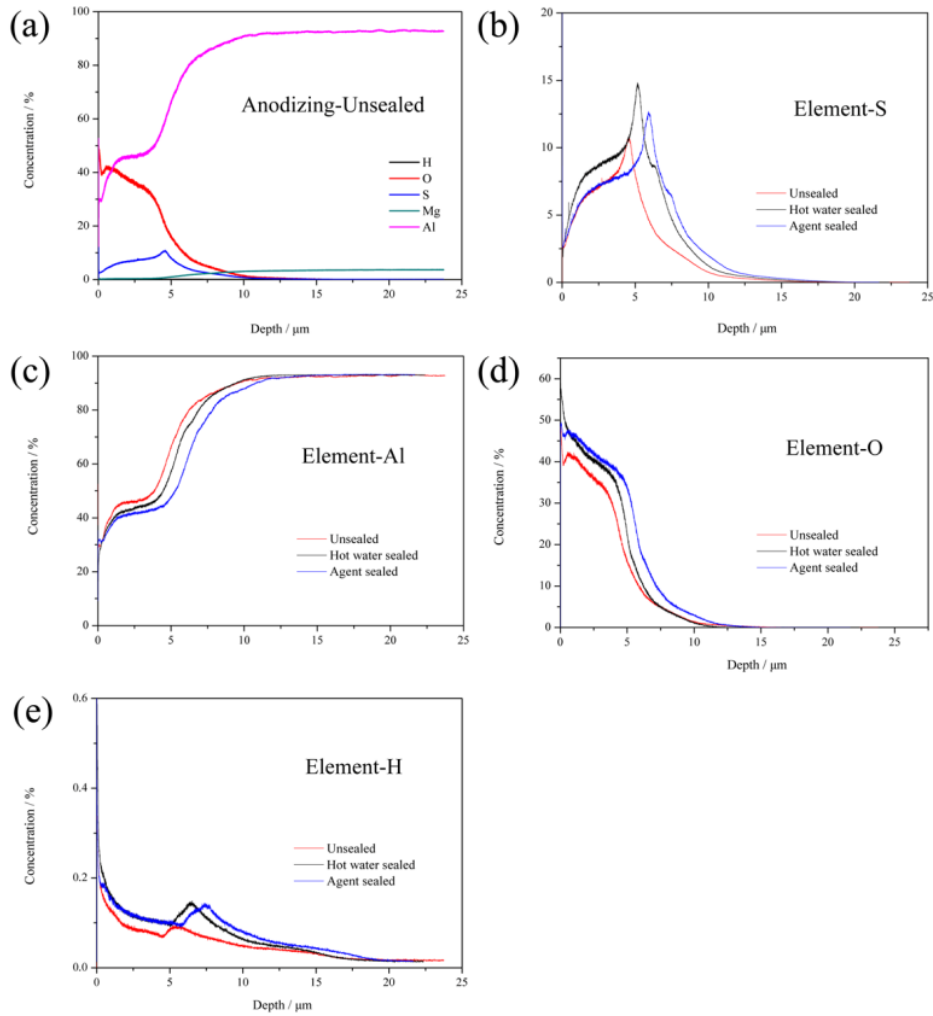


Figure 3. GDOES depth profiles of anodized 5754 aluminum alloy surfaces: (a) unsealed sample, and separate element profiles of (b) S, (c) Al, (d) O and (e) H for Unsealed, Hot water sealed and Agent sealed samples.

Figure 3b shows the distribution of S element of the three types of anodic films. It was observed in these curves that the peak values of sealed samples (agent sealed and hot water sealed) are obviously higher than the unsealed one. This illustrates that the agent sealed sample played the same role with the hot water sealed sample that could prevent the release of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous solution.

The distribution of Al element of the three types of anodic film are totally associated with the film thickness, displaying similar variation (Figure 3c). Meanwhile, the variation of O element shows similar trend as Al element (Figure 3d). It should be noted that the hot water sealed sample shows a significant high concentration of O element at the initial area, about  $<0.5\mu\text{m}$ . That is because two main reactions occur during hot water sealing procedure:





the nano-pores within the oxide film are filled by Al hydroxide as the volume expansive transformation from aluminum oxide to hydroxide. The  $\text{AlO}(\text{OH})$  is the main substance that plugged the nano-pores and the  $\text{Al}_2\text{O}_3 \bullet 3\text{H}_2\text{O}$  is the main composition of the flower shaped Al hydroxide product on the surface as observed above. Thus, the hot water sealed sample shows higher concentration of O element at the initial.

It is also concluded from the two reactions that the H element is the major evidence of how sealing procedure works. The unsealed sample shows the lowest concentration of H element while the two sealed sample show similar results within the pore area (Figure 3e). This was related to the formation of  $\text{AlO}(\text{OH})$  that filled up the pores of the porous layer. However, the hot water sealed sample shows significant high concentration of H element at initial area, about  $<0.5 \mu\text{m}$ . This was also in consistence with the presence of  $\text{Al}_2\text{O}_3 \bullet 3\text{H}_2\text{O}$  as mentioned above. Consequently, it could be deduced that the presence of sealing agent could effectively prevent the formation of  $\text{Al}_2\text{O}_3 \bullet 3\text{H}_2\text{O}$  and maintain the original morphology of the anodic film. Meanwhile, the inner part of the anodic film was effectively plugged similar as the hot water sealed sample.

The bonding property is evaluated by single lap shear testing. Although the eccentricity of the tensile axis of a single lap-shear joint results in transverse and peel stresses, the tensile test results reported here are in terms of maximum strength or stress at break, assuming that the stresses generating in the adhesive layer are uniform. The curves in Figure 4 show that the three types of samples possess similar yield force  $\sim 24 \text{ kN}$  which is associated with the nature property of the base materials.

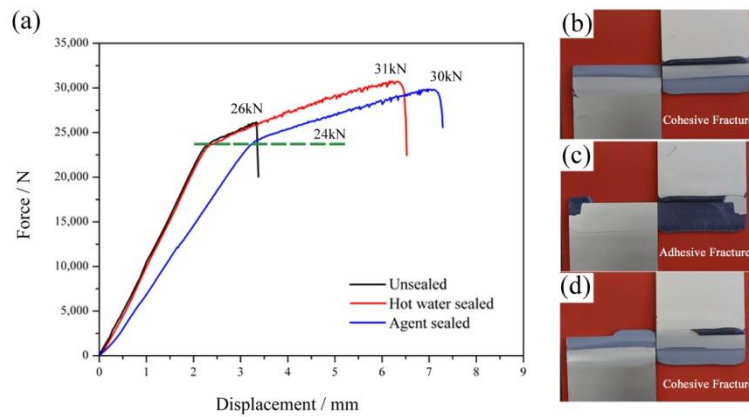


Figure 4. (a) Representative shear force/displacement curves for the samples of different anodizing process, (b) fractured surfaces of unsealed sample, (c) fractured surfaces of hot water sealed sample, and (d) fractured surfaces of agent sealed sample.

However, the hot water sealed sample rapidly fractured after entering into the plastic deformation zone. The fractured surface exhibited an adhesive fracture feature which means the presence of Al hydroxide product on the surface significantly impaired the contact between the adhesive and the anodic film. In contrast, the unsealed samples showed the highest bonding strength,  $\sim 30 \text{ kN}$ . That is because the flowing adhesive could easily penetrate into the nano-pores within the anodic film and after curing the adhesive would retain in the nano-pores that led to a strong bonding strength with the substrate. The agent sealed sample show similar porous structure as the unsealed sample. However, the bonding joint are prone to degradation in corrosive environment and all the three samples will cause corrosion concerns. Therefore, we need to conduct corrosion tests to observe the weather ability of the adhesive joint in the corrosive environment.

Results obtained for lap-shear joints, tested after 50 and 1000 h of ageing in salt spray environment, are shown in Figure 5. The tensile test results of sealed joints (Hot water sealed and Agent sealed) hardly indicate any clear effect of variation from initial strength of the lap joints. The loss of bonding strength is less than 2%, however, the strength of unsealed lap joints were significantly lower than initial strength, indicating a bonding strength loss of nearly 10%. That is because water gradually penetrated into the joint during aging in the humid environment. Bjørgum et al. [15] proposed that water usually works as a plasticizer, leads also to a lower strength at break. The presence of flower shaped Al hydroxide product effectively inhibit the penetration of water. The agent sealed pore which was partially sealed display similar effect. Thus, the unsealed samples do not have weathering resistance in the corrosive environment. In summary, the agent sealed sample has advantages not only for corrosion protection but also for adhesive bonding.

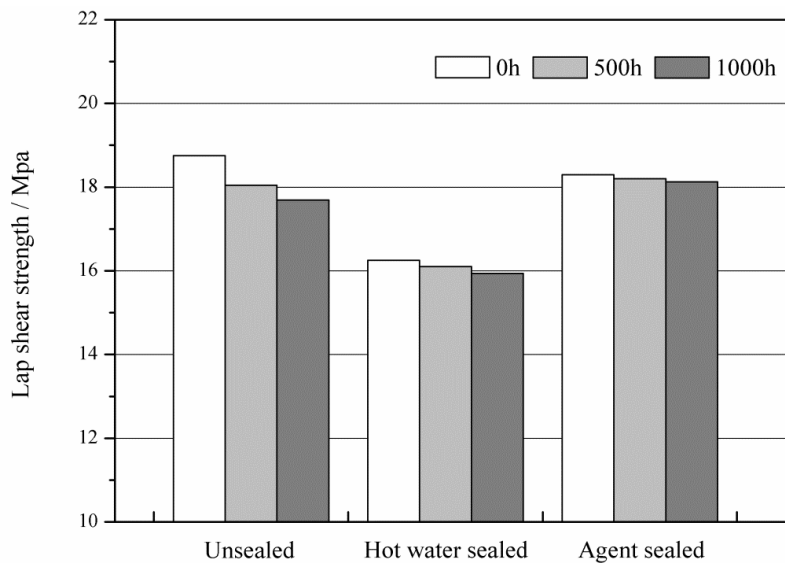


Figure 5. Single lap shear test results obtained for adhesive bonded joints of different anodizing process after 500 and 1000h of exposure in salt spray.

## CONCLUSIONS

The pore structure of anodic films significantly influenced the adhesive bonding performance. The unsealed sample showed porous structure and provided high bonding strength, however, the durability was poor in corrosive environment because the water and aggressive ions could easily penetrate into the porous structure. The hot water sealed sample showed fine and loose structure on the surface. It was mainly composed of  $Al_2O_3 \cdot 3H_2O$  and prevented the direct contact between the adhesive and the anodic film. The bonding strength was low but the durability is relatively high. The agent sealed sample showed porous structure on the surface and the inner layer was filled by  $AlO(OH)$ , and thus, provided both high bonding strength and durability in corrosive environment.

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