Transactions on Engineering Sciences vol 8, © 1995 WIT Press, www.witpress.com, ISSN 1743-3533

Observation of anodic oxide films on aluminium: mechanism of pore closure during hydrothermal treatment and salt spray exposure behaviour

M.C. Sainte Catherine, N. Celati
Centre de Recherches et d'Etudes d'Arcueil, 16 bis, av. Prieur de la Côte d'Or, 94114 Arcueil Cedex, France

Abstract

The transmission electron microscopy study of alumina films formed by anodization of aluminium in chromic bath is reported. The amorphous alumina coating has a duplex microstructure (thick irregular branching porous layer and thin barrier layer). The porous layer morphology depends on the substrate structure (tubular for commercially pure aluminium, irregular branching for aluminium alloys). During the sealing process, the hydration of alumina produces a thickness increase of the pore walls. Then, the wall irregularites induce the formation of bumps leading to a cellular structure of the hydration product which plugs the pores.

1 Introduction

Porous anodic films obtained on aluminium by anodizing in acid electrolytes have received widespread attention owing to their importance in surface treatments of aluminium (corrosion protection and "keying" layer in the adhesive bonding of aluminium parts in aeronautic industries). In such aggressive solutions, a thick porous film is formed. This treatment is followed by a hydrothermal sealing process. Anodized aluminium is dipped in hot water resulting in the conversion of anhydrous alumina to boehmite. This transformation seals the porous structure improving the corrosion protection. This paper deals with the influence of substrate structure upon alumina layer growth in chromic bath, the analysis of the sealing process versus porous layer morphology, the structural changes induced by salt spray exposure.

Transactions on Engineering Sciences vol 8, © 1995 WIT Press, www.witpress.com, ISSN 1743-3533

2 Experimental details

Table 1. Chemical composition of aluminium alloys

wt. %	Cu	Mg	Mn	Cr	Si	Fe	Ti	Zn	Zr	Al
1050	0.013	0.016	0.0035	0.0017	0.14	0.22	0.009	0.019	--	bal.
2024	4.46	1.42	0.65	0.01	0.08	0.17	0.02	0.1	0.01	bal.
6013	1.0	0.94	0.58	--	0.79	0.22	0.03	0.15	--	bal.

Aluminium alloys (Table 1) were anodized in chromic bath. Subsequent dipping in hot water resulted in sealing ratios of about 50, 80 and 100%.

For TEM study, specimens were prepared using sections perpendicular to the film surface (parallelepipeds : 3.0 mm long, 1.5 mm wide, 0.5 mm thick). Those sections were mechanically polished down to a thickness of 30 µm and then ion beam thinned on both sides with argon ions (5 kV, 20° incidence angle).

The sealed anodized alloys were exposed 750 hours to neutral salt spray test (ISO 9227).

3 Results

TEM cross sections revealed the duplex nature of the anodic layer : thick porous layer (few micrometres thick, fig. 1.a,b) and barrier layer (about 40 nm thick) near the ceramic/metal interface (fig. 1.c). The structure of the anodic oxide film is considered as amorphous alumina but having a close relation to γ alumina[1]. Alumina crystallized under electron beam irradiation in the microscope (few minutes) to form γ alumina. This crystallization occurs all the more since alumina is anion-free[1,2,3]. Few amounts of sulphur, chromium and silicon are found in the film. They come from substrate and process bathes.

3-1 Influence of substrate upon growth of alumina porous layer

A pore branching structure was observed as is usual for chromic anodization[4]. In the case of 1050 aluminium (commercially pure aluminium), tubular pores grown quite perpendicularly to the substrate (fig. 1).The mean pore diameter measured in the middle of the film is about 50 nm but a shrinkage of the pores took place at the film surface combined with an increase of the pore density (fig. 1.a). The alumina growth induces a high density of dislocations in the metal due to the release of stresses. At a micrometric scale, a cellular structure has developed (mean diameter of the cellules : 1.4 µm, fig. 1.c). It is difficult to link this particular growth to the aluminium grains (size and crystallographical orientation) whereas some

Transactions on Engineering Sciences vol 8, © 1995 WIT Press, www.witpress.com, ISSN 1743-3533

authors[4] have proposed. Grain size and cellular diameter have the same order of magnitude but grain boundaries and cell boundaries are not systematically combined.

For aluminium alloys, a more irregular branching structure developed by anodizing. This cellular microstructure of the porous layer (fig. 2) results from precipitates in the bulk metal which disrupt the alumina growth. Most of them dissolve giving raise to an additional porosity in the film (6013 alloy, mean pore diameter : 300 nm).

3-2 Influence of porous alumina microstructure upon sealing

Sealing takes place from the consumption of the alumina wall to form hydrated product. For 1050 aluminium, two steps of pore closure were evidenced. For the lower sealing ratios (up to 50%), although a noticeable decrease of the pore diameter occurs, pore geometry keeps the same shape as the unsealed film (Fig. 3(a,b)). Thus, Electrochemical Impedance Spectroscopy (EIS) measurements indicated a same electrical behaviour for those films[5]. This class of sealed films would have an identical behaviour as the unsealed film with regards to adhesion but improved corrosion resistance. As sealing proceeds, the hydration product, boehmite, offering a cellular morphology tends to plug the pores (fig. 3(c,d)). Water can't anymore diffuse down the pore length and a ion transport mechanism through the boehmite may occur. Wall hydration can be affected by different disruptive factors such as species incorporation coming from the bath, gas inclusion (steam, oxygen), pore shape, branching and shrinkage resulting in plugs rather than sealing[6]. Cellular morphology of the hydrated product can also result from damage occurring during sample preparation and observation (vacuum and irradiation) leading to a dehydration of boehmite and micropore formation. The effects of pore shape upon the sealing process were clearly evidenced on cross sections of partially sealed 6013 and 2024 alloys of which initial porous microstructure was irregular (fig. 2,4). Even for a partial sealing of 50 %, the hydration product is already cellular whereas this microstructure was only developed for higher sealing ratios in the case of 1050 aluminium.

As expected, sealing resulted in the decrease of the anhydrous barrier coating thickness (fig. 5).

3-3 Salt spray exposure behaviour

For high sealing ratios of the aluminium alloys, the hydrated alumina film is composed two layers separated by a depletion area (fig 6). The bottom layer kept its original alumina skeleton whereas the upper layer appeared to have undergone a complete hydration. This upper layer is differently textured from the inner regions : less dense filamentous area (fig. 6(b)). No degradation of the samples were visible at the end of the test period while clear different behaviours were detected by EIS[5] corresponding to an

Transactions on Engineering Sciences vol 8, © 1995 WIT Press, www.witpress.com, ISSN 1743-3533

increase of the porosity of the sealed layer. TEM observations of the tested samples revealed a decrease of density in the upper layer (fig. 6 b,c). No significant changes were observed in the bottom layer but TEM investigations will be carried on to improve microstructural corrosion damage knowledge and correlated with EIS data.

4 Conclusions

TEM has been successfully applied to determine the influence of the substrate upon the oxide growth and the mechanism of pore hydration and closure during hydrothermal treatment used to improve corrosion resistance of aluminium. During the first steps of the sealing process, growth of the hydrated product along the pore wall occurs, keeping roughly the initial pore geometry. Then due to pore shape, internal surface pore topography, pore shrinkage in surface, branching, bath incorporated species, plugs are formed retarding hydration process. A medium sealing would be preferred for surface preparation providing to the aluminium substrate both corrosion resistance and "keying" function with regards to painting or bonding.

References

1. Ono, S., Ichinose, H., Kawaguchi, T.& Masuko N. The observation of anodic oxide films on aluminum by high resolution electron microscopy, *Corrosion Science*, 1990,. **31**, 249-254.
2. Ono, S., Ichinose, H. & Masuko, N The high resolution observation of porous anodic films formed on aluminum in phosphoric acid solution, *Corrosion Science*, 1992, **33** (6), 841-850.
3. Shimizu, K. Thin Surface films on metals and alloys, *Corrosion Science*, 1993, **35**, 247-252.
4. Berbezier, I.,. Romand, M.& Kuntz, J. M. Adhesion primer properties, microstructural changes induced by ageing, *Journal of Adhesion*, 1990, **33**, 5-18.
5. Celati, N, Sainte Catherine, M.C., Keddam, M.& Takenouti, H., to be published in Materials Science Forum, *Proceedings of the International Symposium on the Electrochemical Methods in Corrosion Research,* Sesimbra, Portugal, 1994.
6. Patermarakis, G. & Papandreadis, N., Effect of the structure of porous anodic Al2O3 films on the mechanism of their hydration and pore closure during hydrothermal treatment, *Electrochemica Acta*, 1993, **38** (10), 1413-1420.

Acknowledgements : Thanks are due to Y. L'Aminot, trainee student for his participation in TEM study.

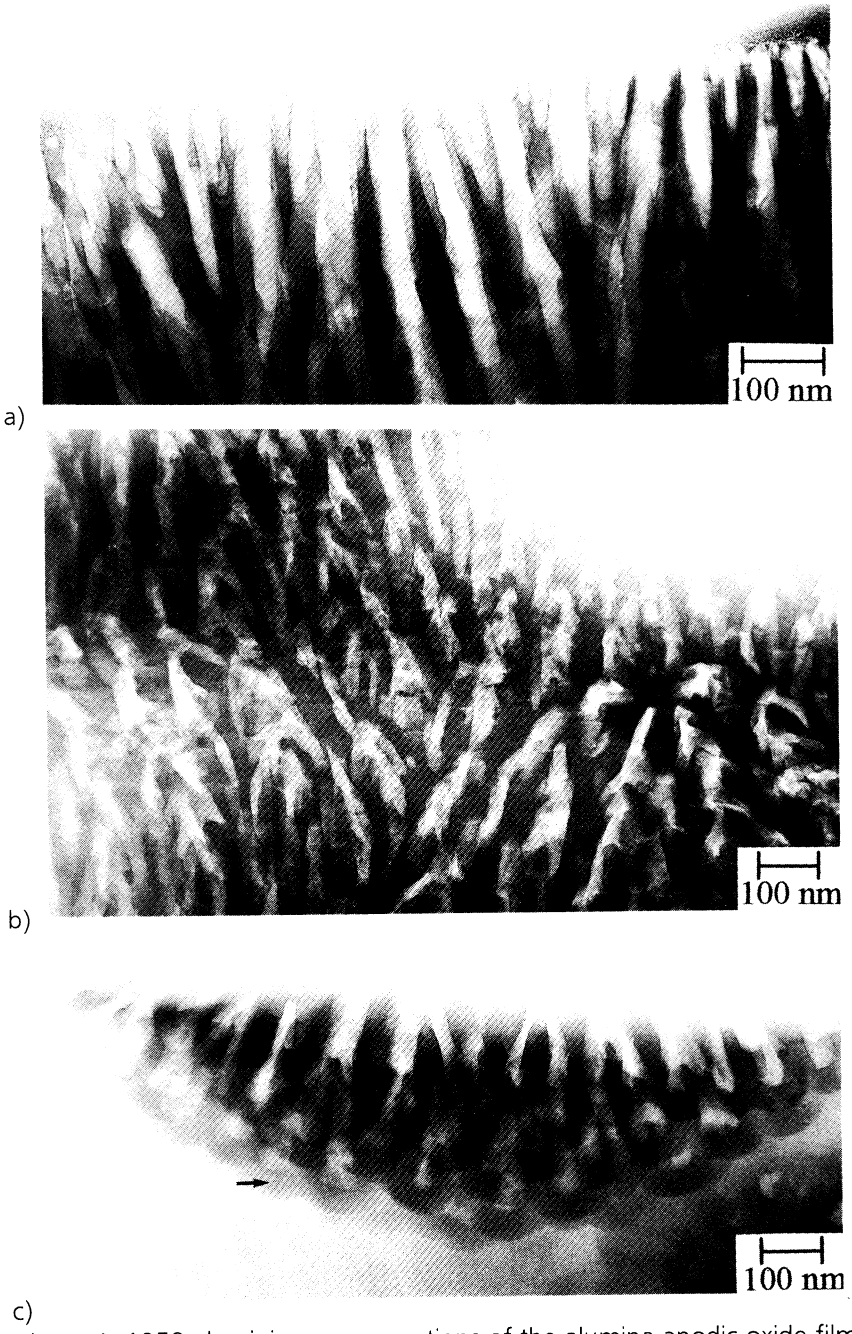

Figure 1: 1050 aluminium, cross sections of the alumina anodic oxide film a) top of the film, b) middle of the film, c) aluminium/oxide interface (arrow indicates the barrier layer)

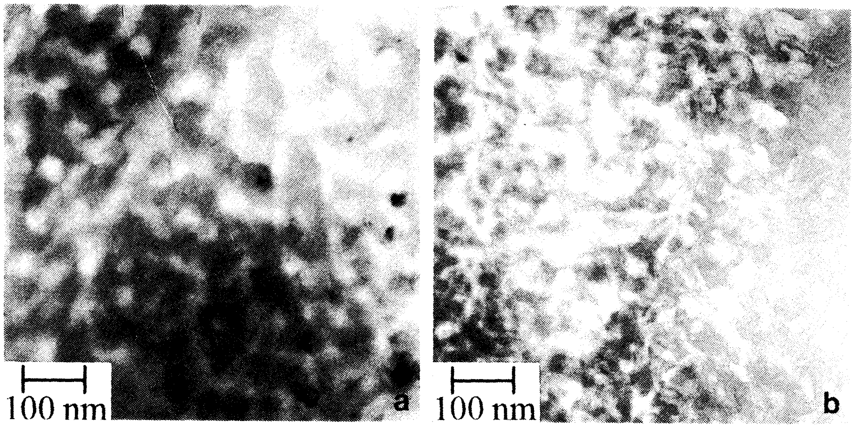

Figure 2 : Cross sections of the alumina anodic film a) 6013, b) 2024 alloys

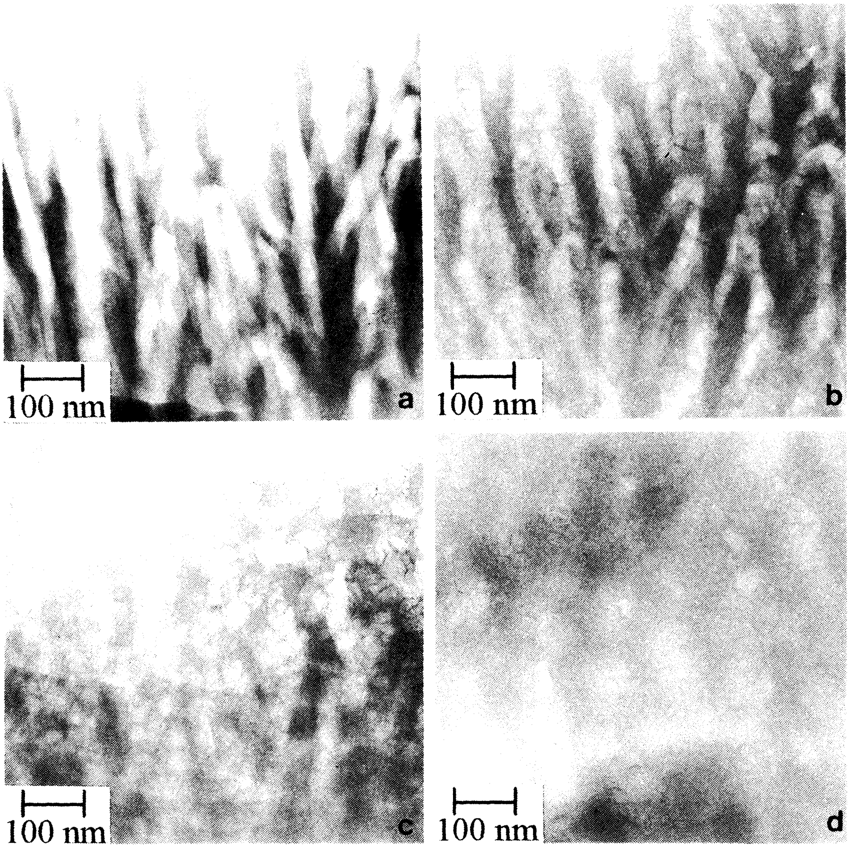

Figure 3 : 1050 aluminium , cross sections of the alumina anodic film a) unsealed, b) partially sealed 50 %, c) partially sealed 80 %, d) sealed

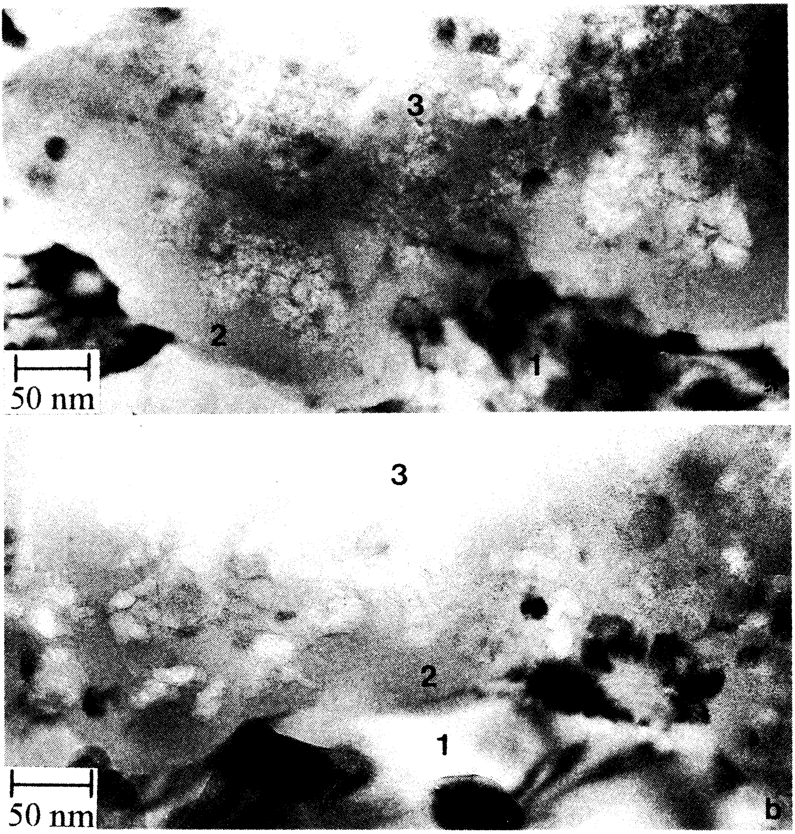

Figure 4 : Cross sections of the partially sealed alumina anodic film, a) 6013, b) 2024 alloys ; 1 : aluminium alloy, 2 : barrier layer, 3 : porous layer

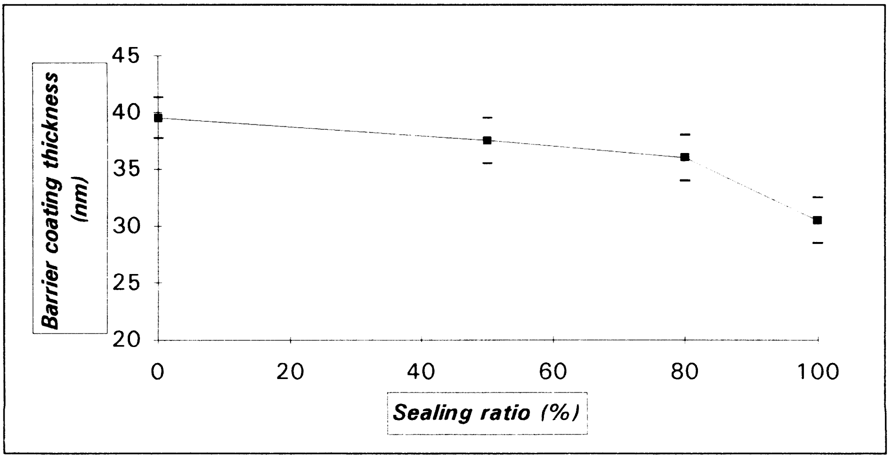

Figure 5: Anhydrous barrier coating thickness versus sealing ratio

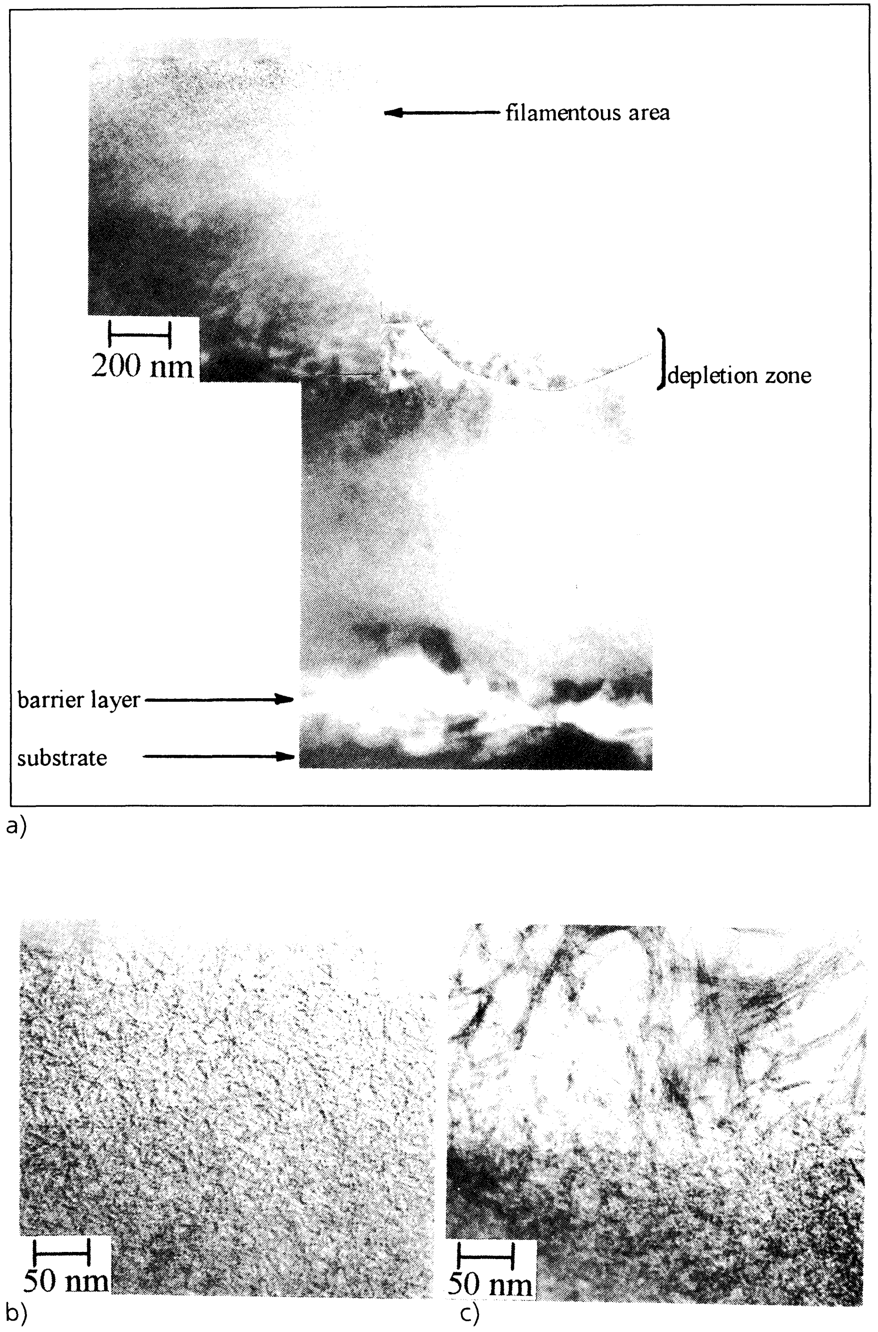

Figure 6 : Cross sections of the 2024 anodic film a, b) as sealed, c) after salt spray exposure