Corrosion Behaviour of Environmentally Friendly Treatments for Aluminium Alloys

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Abstract. In this paper an alternative anodising procedure, that confers a good base for painting and adhesive bonding of aluminium, is envisaged to replace the chromic acid anodising The substrate consisting of Al 2024-T3 is immersed in a cerium solution in order to create a cerium-containing film that covers the copper rich precipitates, followed by anodising in a boric acid-sodium borate/sulphuric acid solution. The results showed that this procedure confers good corrosion protection to the substrate and can potentially constitute an alternative to the Cr-VI based treatment.

Introduction

Painting and adhesive bonding of aluminium are essential technologies in many industrial sectors (e.g. aerospace industry) and each process depends on the generation of a strong and stable interface between an organic layer and the surface consisting of naturally formed metal oxide. Pre-treatments on the substrates, which leave the metal with an oxide structure that is stable and compatible with the organic layer, are vital to achieve the desirable levels of strength and reliable long-term performance and have been used for decades. However, they involve a range of environmentally objectionable chemicals, such as solvents and chromates, thus needing to be replaced.

Several attempts have been made to replace the Cr (VI) – based treatments. In the present work the traditional chromic acid anodising was replaced by a boric acid-sodium borate/sulphuric acid bath. The alloy was pre-treated in a cerium nitrate solution, in order to form a film that covers the copper rich precipitates of the alloy, which impair good anodising.

Experimental

Aluminium alloy 2024-T3 coupons were used. The specimens were degreased with tricloroethylene (4 min), followed by etching in 3 $g.l^{-1}$ NaOH solution (8 min) and desmutting in 50% v/v HNO_3 solution (30 sec). The anodising bath (ABS) consisted of a mixture of H_2SO_4 (15%) with a solution containing 0.5M H_3BO_3 and 0.05 M $Na_2B_4O_7.10H_2O$, in the proportion 70/30 (v/v). The optimised temperature and current density were respectively 40ºC and 2 $A.dm^{-2}$ and the anodising time was 30 minutes. The choice of 40ºC came from the fact that lower temperatures lead to higher coating thickness, which should be deleterious for fatigue resistance. The anodising was performed on as-etched surfaces and on surfaces also pre-treated by immersion in 0.01M $Ce(NO_3)_3$ solutions for 4 hours.

After anodising the specimens were sealed in boiling distilled water for 30 minutes. However, before sealing the specimens were observed on a field emission scanning electron microscope (SEM), on the surface and in a section almost perpendicular to the surface. This latter observation also allowed the determination of the coating thickness.

Since the fatigue is an important property of these materials, fatigue tests were carried out on anodised specimens. For comparison, fatigue resistance was also obtained on as received and chromic acid anodised specimens. The alloy was submitted to tensile-tensile fatigue tests in air and at the environmental temperature, in order to obtain S-N plots. The tests were carried out according to ASTM E 466-82 [1], using an INSTRON 8502 servo-hydraulic machine.

The corrosion behaviour was studied in 3% NaCl solution by Electrochemical Impedance Spectroscopy, using a Solartron 1250 frequency response analyser connected to the cell via a Solartron 1286 electrochemical interface.

Results and Discussion

Figure 1a shows a SEM photograph of the transverse section of the specimen anodised in the ABS. It allows the determination of the coating thickness that is approximately 2.5 μm. Higher magnification micrograph (160 000 ×, Fig. 1b) shows in more detail the structure of this coating. Linear continuous pores perpendicular to the specimen surface, as those reported in the literature for anodised aluminium, cannot be seen. The coatings have a grain like structure with the grains separated by pores. The grains seem to have grown preferentially in one direction, revealing a lamellar shape.

Coatings formed after pre-treatment in cerium solutions were also observed by SEM. The structures observed were similar to those previously reported, apart a finer structure with smaller grains. The presence of a barrier layer in contact with the metallic surface could not be detected in both cases, which indicates that it should be very thin.
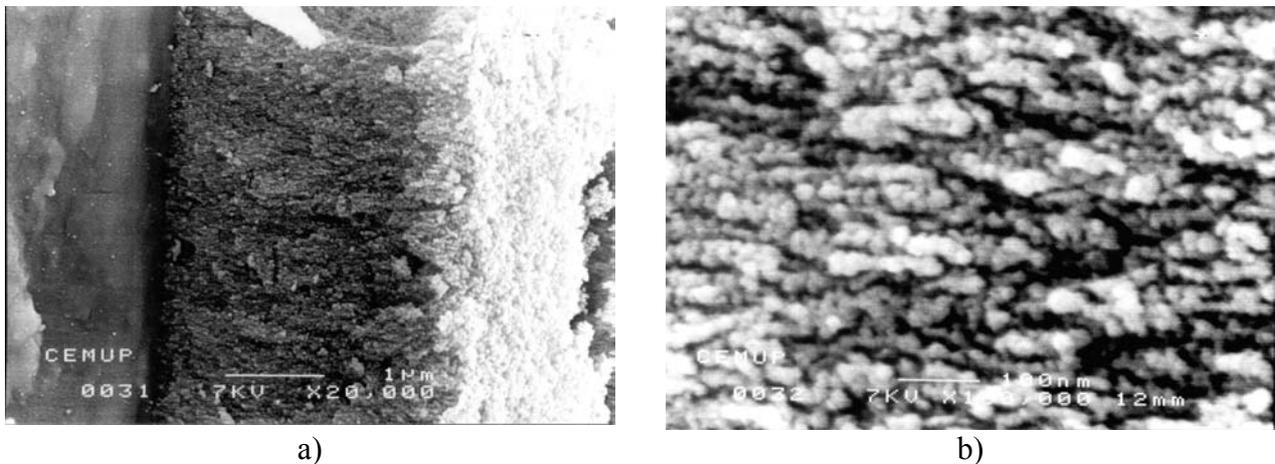

a) b)

Figure 1. Micrographs of transverse sections of anodised Al 2024-T3 in ABS:
a) 20 000×.; b)160 000 ×

The impedance results for 1 day and 7 days immersion in 3% NaCl solution for ABS anodising are shown in Fig. 2a. The impedance values do not change significantly with time, which reveals a good corrosion performance of the specimen.

As a plateau is not usually observed at low frequencies for anodised samples that show even pitting or pronounced corrosion, practical criteria have been established to assess the corrosion behaviour of this material [2-4]. Most of them are based on the value of the impedance in the low frequency region. Thus, according to Mansfeld and Kendig [2], a damage function, D, which is defined as

$$D = \log \left(\frac{Z_o}{Z_t} \right)_{0.1Hz} \tag{1}$$

is a useful measure of the corrosion susceptibility. Z_o and Z_t are the initial impedance values and the values for $t = t_{corr}$ at 0.1 Hz, respectively. The value of t_{corr} was considered 7 days and a value of $D = 0$ represents perfect corrosion behaviour. The present authors used as criterion in previous work [4] the value of the impedance taken at $\omega = 10^{-1}$ rad.s^{-1}, after 7 days of immersion in the testing solution. If this parameter is larger than 10^6 Ω.cm^2, the coating is considered to have enough corrosion resistance for practical applications. According to this latter criterion, the value of log |Z| was monitored during 7 or more days. The above criterion was fulfilled, since that parameter was always higher than 6.5.

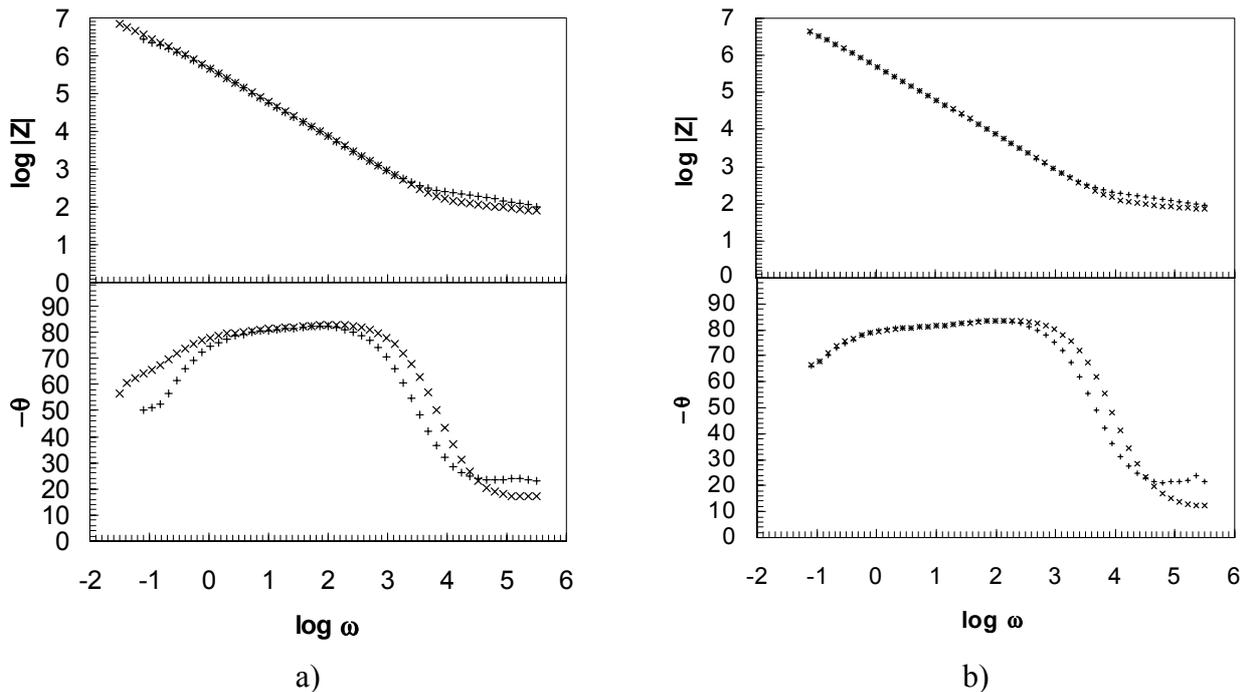a)   b)

Figure 2. Bode diagrams for specimens anodised in ABS solution, after ✕ = 1 day and + = 7 days of immersion in 3% NaCl solution: a) without pre-treatment; b) pre-treated with cerium

The effects of pre-treating the alloy with cerium nitrate were also assessed by EIS. These compounds are reported to be inhibitors [5,6] and there was an interest in checking whether or not they improve the quality of the coating, although its corrosion behaviour was considered already good. For cerium treated specimens there is a perfect coincidence in the low frequency range of the spectrum after 7 days and the spectrum after 1 day of immersion (Fig. 2b). Thus it seems that cerium has a positive effect. SEM observations showed that the porous layer has a finer structure with smaller pores and more uniformly distributed. Moreover, scanning Auger maps obtained on the alloy surface for O, Al, Ce and Cu (not presented) show that a cerium-containing film seems to deposit preferentially on the copper- rich precipitates of the alloy, which could avoid the evolution of oxygen that impairs anodising.

Fig. 3 depicts the S-N plot obtained for specimens anodised with the ABS in tensile-tensile fatigue tests up to the fracture of the specimen. Force sine waves with a stress ratio $R = F_{min}/F_{max} = 0.001$ were applied. The frequency changed between 10-25 Hz. In the same figure and for comparison the same kind of plots obtained for the as-received alloy and standard chromic acid anodising are also displayed. The results marked with arrows correspond to specimens that did not break up to 7×10^6 cycles.
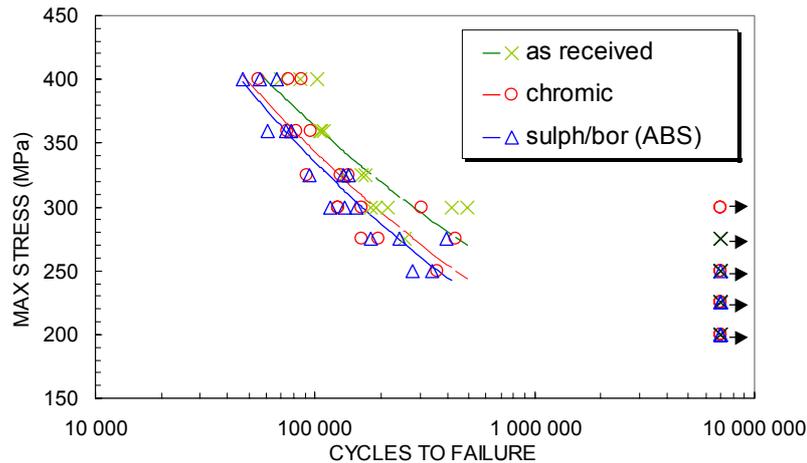
Figure 3. S-N plots obtained for Al 2024-T3 in three different surface conditions: as-received, chromic acid anodised, ABS anodised.

The scattering of the results is typical of S-N plots for alloys of the type under study. From the analysis of the plots it is apparent that anodising induces a decrease of the fatigue resistance. The larger difference in behaviour is observed for stresses below 290 MPa. Comparing the ABS bath with the chromic acid bath it can be noticed that the specimens produced with the former are those that resist to lower maximum stresses. However, in any case the decrease in fatigue resistance is very low. This decrease can be characterised as $(S_{ref}-S)/S_{ref} \times 100$, where S_{ref} is the value of stress to fracture at 10^5 cycles for the reference treatment and S is the same value for the new surface condition. In particular, for ABS anodising relatively to chromic acid anodising, this ratio is ~2%, which is much lower than the scattering range of the results.

Conclusions

- As revealed by EIS, the corrosion resistance of the coating fulfils the practical criterion established for acceptance.
- Pre-treating the surface with cerium salts leads to an improvement of the corrosion resistance.
- The fatigue resistance of the ABS anodised specimens is slightly lower (~ 2%) than the chromic acid anodised ones, although this difference is within the experimental scattering of the results.

References

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