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Behaviour of anodised aluminium in very long-term atmospheric exposure

E. Escudero *, V. López, E. Otero, M.J. Bartolomé, J.A. González

National Centre for Metallurgical Research (CENIM), Spanish National Research Council (CSIC), Avda. Gregorio del Amo, No. 8, 28040 Madrid, Spain

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Abstract

This communication analyses the behaviour of anodised aluminium specimens, with different degrees of sealing in deionised water and acetate solutions, exposed for 25 years to the Madrid atmosphere. Changes in physical–chemical properties as a function of ageing are assessed using traditional standard quality control tests, electrochemical impedance spectroscopy (EIS) and optical and electron microscopy, and durability is estimated on the basis of gravimetric data. The results allow, for atmospheres of moderate aggressivity, such as the case of the CENIM in the University City of Madrid, service lifetimes of 100 years or more to be predicted for the usual anodic film thicknesses in architectural applications. If the localised corrosion process is not initiated, the quality of anodic films improves with ageing, in contrast to what happens with the rest of protective coatings.

Keywords: Aluminium; EIS; Weight loss; Anodic films; Atmospheric exposure

1. Introduction

In many natural environments, aluminium and its alloys show excellent resistance to atmospheric corrosion, with average corrosion penetrations of less than 1 μm/year [1], typical of the passive state. This insignificant attack is, however, sufficient to significantly deteriorate the appearance of these materials; a property that is highly appreciated in the architectural applications for which they are most widely used. In order to preserve their appearance, aluminium alloys are either lacquered or anodised and sealed. This communication only considers the case of anodic coatings. Industrial approval of anodised aluminium for architectural applications is based almost exclusively on the requirement of a minimum coating thickness, which varies according to the environmental aggressivity [2], and a certain degree of sealing. Both can be checked in production lines by means of very simple quality control tests that are included in the standard codes of most countries [3].

Anodic films retain much less soiling than bare aluminium and their comparatively greater hardness facilitates cleaning operations [4]. This, together with their decorative properties, based on their porous nature and enormously enhanced by colouring and sealing operations, explains their rapid industrial expansion since their introduction more than 70 years ago.

There are no short laboratory tests that allow the long-term behaviour of anodic films in a wide range of environmental conditions to be predicted since correlation with service behaviour has not been demonstrated. Thus, it is necessary to resort to very long exposure tests in more or less corrosive environments in order to obtain significant results. This explains why relevant data are not abundant in the specialised literature [5–13]. There are references that report the conservation of an acceptable appearance by aluminium panels exposed for 40–50 years in urban atmospheres in the United Kingdom [5] and quantitative indications from 10-year tests relating to thickness losses of 0.4–0.6 μm/year in marine atmospheres, reaching concerning values of up to 0.7–0.9 μm/year in industrial environments [6]. Much more satisfactory results are arrived at in atmospheres of low or moderate aggressivity in New Zealand, with penetrations of between 0 and 0.15 μm/year in 12 year tests [7], practically coinciding with values recorded in the Madrid atmosphere for exposure periods of 17 and 20 years [8,9]. Other authors note that corrosion – when it takes place – is localised, in the form of pitting, and that the thickness of the anodic film has a very pronounced effect on the initial induction period, the frequency of pitting and the time taken to reach a predetermined degree of deterioration [10–13]. In strongly industrial atmospheres the

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* Corresponding author. Tel.: +34 9 1 5538900; fax: +34 9 1 5347425.
E-mail address: mebaquero@cenim.csic.es (E. Escudero).

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conservation of appearance can only be guaranteed for 10 years or more by anodic film thicknesses of ≥25 μm [11–13].

2. Experimental methodology

2.1. Materials

The material used in this work is the 1050 aluminium alloy of 99.5% purity, cut into 100×50 mm rectangular specimens of 1.5-mm thickness.

The specimens were degreased by submerging them for 5 min in an aqueous dissolution of phosphoric and cromic acids at concentrations of 250 g/L and 55 g/L, respectively, at a temperature of 30–40 °C. They were then etched by chemical attack in an aqueous solution of 100 g/L sodium hydroxide at 40 °C for variables times, and desmutted by immersion for a few seconds in the aqueous solution of sulphuric and chromic acids. The specimens were thoroughly rinsed with running water between each treatment. Anodising was carried out for 45 min in an electrolyte of 180 g/l sulphuric acid, stirred with compressed air, at a current density of 1.5 A/dm^2. Coating thicknesses of 18–20 μm were obtained.

Sealing was always carried out at boiling point in deionised water, the traditional hydrothermal sealing (HTS), or in deionised water with 0.5 g/l acetate anion, added in the form of sodium or ammonium acetate. The sealing times applied were 0, 1, 5, 10 and 20 min. For some conditions it also has HTS data for 45 min.

2.2. Test methods

The assessment of sealing quality was carried out using standard routine production control methods, the dye spot and 1 kHz admittance tests [3], and by electrochemical impedance spectroscopy (EIS), which has proven to be a rational method for obtaining detailed information on the degree of sealing and the influence of ageing – or any other factor – on the integrity and physical characteristics of the porous and barrier layers [14–16]. The impedance measurements were made in unstirred, aerated 3.5% K_2SO_4 solutions at room temperature, and over a wide frequency range (100 kHz to 1 mHz). The surface acting as working electrode was 1 cm^2 in area and delimited by means of insulating tape for corrosion tests. The EIS cell and instruments used were described elsewhere [8].

The specimens were exposed at an angle of 45°, in 1975, in standard racks installed on the roof of the CENIM. This testing station has an average temperature and relative humidity of 13.8 °C and 60.6%, respectively, with 0.220 as annual fraction of time wetness. The corrosivity category estimated from these values according ISO standard 9223 [17] is C2.

Gravimetric techniques to know the wear of anodic coatings in time, transmission electron microscopy (TEM) to establish the microstructure of the anodic coatings and energy dispersive X-ray analysis-scanning electron microscopy (EDX-SEM) to quantify its composition and optical microscopy to determine the morphology and penetration of localised corrosion when this occurs have been used. Prior to gravimetric tests the specimens were degreased, rinsed with deionised water and dried with compressed air.

3. Results

Fig. 1 shows the evolution with exposure time to the Madrid atmosphere of the mass change of specimens, anodised and sealed, in deionised water (a) and in deionised water with 0.5 g/L acetate anion (b), added in the form of ammonium acetate, respectively. The absorption capacity conserved by unsealed or insufficiently sealed films explains the mass gain that they experience during the initial exposure period, which continues until the pores become saturated with water. The final mass gain is practically the same for all the specimens, irrespective of their sealing time, as can be seen in Fig. 2, since the complementary amount of water to fill the pores is absorbed during exposure. After 2 or 3 years, a slight mass loss starts to be detected, which becomes very evident for ageing times of 10 years or more.

Gravimetric results, such as those shown in Fig. 1, are used to calculate the average thickness losses of anodic films as a function of their sealing time and the type of solution used in the sealing operation. The mass loss is transformed in thickness loss accepting a density of 2.6 g/cm^3 suggested for the sealed anodic coatings (or autosealed during one or more years) [18]. As can

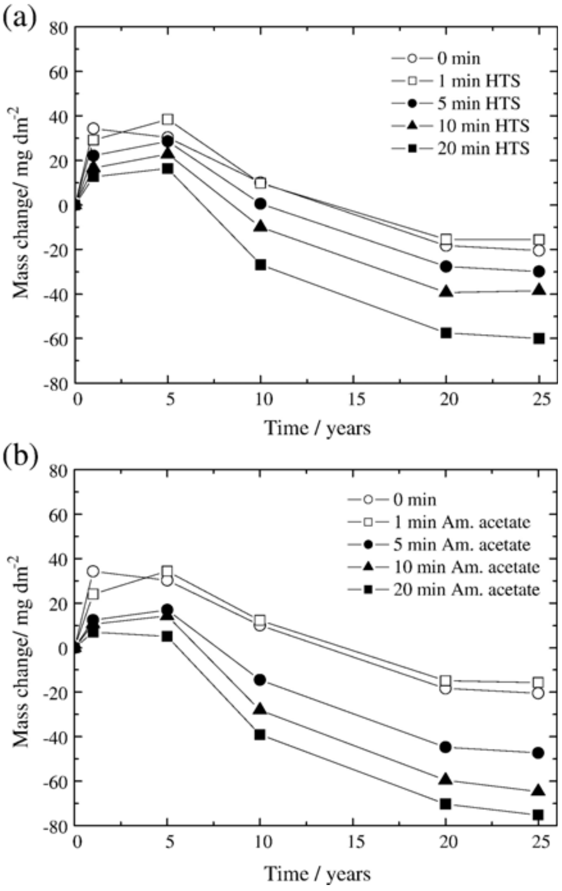

Fig. 1. Mass variation with ageing as a function of sealing time in boiling deionised water (a) and in boiling deionised water with 0.5 g/l acetate addition, in the form of ammonium acetate (b). The initial value includes the water absorbed during sealing.