INFLUENCE OF ALLOYING ELEMENTS AND ETCHING TREATMENT ON THE PASSIVATING FILMS FORMED ON ALUMINIUM ALLOYS

S. Feliu (Jr)^{*} and M.J. Bartolomé

Centro Nacional de Investigaciones Metalúrgicas (CENIM), CSIC, Avda. Gregorio del Amo, 8,
28040 Madrid, Spain

^{*}Corresponding author: Tel.: +34 915538900; fax: +34 915347425

E-mail address: sfeliu@cenim.csic.es (S. Feliu, Jr)

ABSTRACT: This paper studies the characteristics of aluminium oxide layers present on the surface of commercial aluminium specimens after thermomechanical processing and after subsequent etching in an alkaline solution, highlighting the main differences observed. An attempt is made to establish possible relationships between alloying elements and the characteristics of these layers.

Keywords: Aluminium, oxide films, alloying elements, surface treatments.

1. INTRODUCTION

Aluminium is a soft, ductile metal, but when alloyed with other elements its physical and mechanical properties can be substantially modified to produce valuable engineering materials. Typical alloying elements for aluminium are copper, magnesium, silicon, iron, zinc and titanium. An important aspect of aluminium and its alloys is the growth of a thin passivating oxide layer that forms immediately when a fresh surface is exposed to the air. In dry air, at room temperature, the oxide reaches a limited thickness of about 4 nm, but oxidation in a moist atmosphere and/or at a higher temperature increases the oxide thickness [1]. Al_2O_3 has many desirable qualities, which include being chemically inert over a fairly broad pH range, having high hardness, and possessing certain barrier properties [2].

The chemical composition and physical characteristics of the oxide layer affect many of the metal's properties, including its wettability, adhesion performance and corrosion resistance [3-9]. The composition and the thickness of the oxide can vary widely depending on the specific alloy composition and the manufacturing conditions (i.e. rolling conditions, heat treatments, anodising and chemical etching process, etc.). A knowledge of the composition and the thickness of this oxide layer is vital for a better understanding of relationships between the surface structure and the properties of aluminium materials [10].

There is a significant interest in the response of aluminium and its alloys to alkaline pretreatment in view of their wide commercial use and the need for surface cleaning prior to architectural, automotive, aerospace or packaging applications, etc. Many commercial aluminium alloys, which frequently contain relatively high levels of elements that give rise to the presence of a second-phase material, are subjected to alkaline etching in order to remove mill scale, residual oil and sub-surface defects [11]. Alkaline etching in a NaOH solution is a normal operation in aluminium anodising.

The present research focuses attention on surface oxide films resulting from the thermomechanical processing and the chemical pretreatment (alkaline etching) applied to aluminium alloys before anodising. The study forms part of a general exploration of the

influence of alloy composition on the formation of anodic films in sulphuric acid currently under way [12].

In this work X-ray photoelectron spectroscopy (XPS) has been used to compare the nature and the content of alloying elements and impurities on the surface of various commercial aluminium alloys after thermomechanical processing, and oxide film thicknesses, with results obtained after an etching process and prolonged exposure to the laboratory atmosphere.

2. EXPERIMENTAL PROCEDURE

2.1. Al alloys

The chemical composition of the tested aluminium alloys is shown in Table 1 (weight percentages). The copper content is 4% wt. in the Al-Cu aluminium alloy and less than 0.04% wt. in the rest of the alloys. The Mg contents in the Al-Cu and Al-Mg-Si aluminium alloys are between 0.6 and 0.8% wt. Attention is drawn to the presence of a Mg content of close to 3% wt. in the Al-Mg aluminium alloy. The relatively high sodium impurity contents may be associated with contamination introduced in the alloys through the aluminium and magnesium [13] used during the melting and casting process. The Al-Cu was aged to T4 temper condition, the Al-Mg-Si alloy was artificially aged to T6 condition and the Al-Mg alloy was in O/H111 condition.

2.2. Etching of specimens

The specimens were degreased by submerging them for 5 minutes in an aqueous dissolution of sulphuric acid and chromic acid in concentrations of 15% vol. and 5% wt., respectively, at a temperature of 30-40 °C. They were then etched in an aqueous solution of 10% sodium hydroxide at 40-50 °C for 5 min. and were neutralised by immersion for a few seconds in the degreasing dissolution. After each treatment the specimens were thoroughly rinsed in running water and dried with compressed air.

2.3. Surface analysis

Photoelectron spectra were recorded using a Fisons MT500 spectrometer equipped with a hemispherical electron analyser (CLAM 2) and an Mg K α X-ray source operated at 300 W. The samples were mechanically fixed on small flat discs supported on an XYZ manipulator placed in

the analysis chamber. The residual pressure in this ion-pumped analysis chamber was maintained below 10^{-8} Torr during data acquisition. The spectra were collected for 20-90 min., depending on the peak intensities, at a pass energy of 20 eV, which is typical of high-resolution conditions. The intensities were estimated by calculating the area under each peak after smoothing and subtraction of the S-shaped background and fitting the experimental curve to a mix of Lorentzian and Gaussian lines of variable proportions. Although specimen charging was observed, it was possible to determine accurate binding energies (BE) by referencing to the adventitious C1s peak at 285.0 eV. Atomic ratios were computed from peak intensity ratios and reported atomic sensitivity factors [14].

For the acquisition of concentration profiles (distribution of elements as a function of specimen thickness) the surface was sputtered by argon ion bombardment (AIB). Bombardment was performed using an EXO5 ion gun incorporated in the equipment, provided with a scanning unit to track the beam operating at a voltage of 5 kV, an intensity of 10 mA and a pressure of 1×10^{-7} Torr. The sample current was 1 μ A during bombardment.

3. EXPERIMENTAL RESULTS

3.1. Analysis of outer surface of aluminium alloys after thermomechanical processing

Table 2 shows the element compositions obtained by XPS on the aluminium alloy surfaces after thermomechanical processing. Attention is drawn to the presence of significant amounts of Mg on the Al-Cu, Al-Mg-Si and Al-Mg alloys. The Mg/(Mg+Al) atomic ratios obtained by XPS in the Al-Mg-Si alloy reach values close to 0.25, suggesting that magnesium covers approximately 25% of the aluminium surface. The atomic percentages of magnesium obtained by XPS on the aluminium alloy surfaces after thermomechanical processing seem to be largely independent of the Mg content in the bulk alloys (Table 2). It is interesting to point up the absence of Cu on the surface of the Al-Cu alloy after thermomechanical processing, and also the absence of significant amounts of Si, Fe, Mn and the rest of the elements present in the bulk of the tested alloys.

Figures 1a-1d show Al2p high resolution XPS spectra obtained on the original aluminium alloy surfaces after thermomechanical processing. The spectrum observed on the pure Al specimen shows the most intense component at a binding energy of 74.6 eV, associated to the presence of aluminium in the form of aluminium oxide, and a less intense component at a binding energy of 71.7 eV, which may be attributed to the presence of aluminium in metallic state (Fig. 1a). Figure 1b shows the Al2p high resolution XPS spectrum obtained with the Al-Cu alloy. Attention is drawn to the presence of a new component that appears at a binding energy of 72.7 eV. In the literature [15,16], the presence of an intermediate component in the spectrum taken from an oxidized aluminium surface has been tentatively interpreted as being due to a not-completely oxidized Al-phase.

It is interesting to note that while the most intense component of the Al2p spectra for the pure Al and Al-Cu specimens appears at a binding energy of 74.6 eV (Fig. 1a and 1b), on the Al-Mg-Si specimen the most intense component is observed at a lower binding energy (71.7 eV), associated with the presence of aluminium in metallic state (Fig. 1c). The Al2p spectrum obtained on the surface of the Al-Mg specimen (Fig. 1d) shows the most intense component at a binding energy of 74.6 eV, associated with the presence of aluminium in the form of aluminium oxide.

Figure 2a shows the Mg2p high resolution XPS spectrum obtained on the outer surface of the Al-Mg-Si alloy after thermomechanical processing. This spectrum is representative of the Mg2p spectra observed on the surfaces of the Al-Cu and Al-Mg alloys. The spectrum contains one single component with a binding energy of 50.0 eV, which is typical of magnesium as MgO.

3.2. Concentration profiles of aluminium specimens after thermomechanical processing

The evolution with argon ion bombardment time of the Al2p high resolution XPS spectra obtained on the surface of the various aluminium alloys is presented in figure 1a-1n. On the Al-Cu and Al-Mg specimens (Fig. 1b, 1f, 1i, 1l and 1d, 1h, 1k and 1n, respectively) a high aluminium content in the form of Al₂O₃ is detected even at bombardment times of 30 minutes (removed layer thickness close to 60 Å). Figure 2a-2d show the evolution with argon ion

bombardment time of the Mg2p high resolution XPS spectrum corresponding to the Al-Mg-Si specimen. The spectra obtained are fairly similar, containing one single component at a binding energy of 50.0 eV. On the other hand, no appreciable Cu signal is observed in the Cu2p high resolution XPS spectra obtained on the surface of the Al-Cu alloy after thermomechanical treatment, even after argon ion bombardment (Fig. 3a-3d).

A precise measurement of the thickness of the Al₂O₃ layer resulting from thermomechanical processing has not been possible due to the presence of MgO islands on the outer surface of the Al-Cu, Al-Mg-Si and Al-Mg alloys, which results in the absence of significant changes in the $I_{\text{oxide}}/I_{\text{metal}}$ ratio (proportional to the oxide layer thickness), even at AIB times of as long as 30 minutes (Fig. 1).

3.3. Analysis of the outer surface of aluminium alloys after the etching process

Figure 4 shows the general XPS spectra obtained on the outer surface of the various aluminium alloys after chemical etching. Attention is drawn to the presence of Na on the Al-Mg alloy surface. Table 3 shows the elemental composition obtained by XPS on these surfaces. Besides the presence of Na on the Al-Mg alloy and the expected presence of O and Al, it is to point out the not detection of any of the other elements that accompany Al in the bulk analysis of the alloys.

Figure 5a-5d shows the Al2p high resolution XPS spectra. Each spectrum contains two components, which may be associated to the presence of metallic Al (71.7 eV) and oxidised Al (74.6 eV).

Figure 2e-2h shows the Mg2p high resolution XPS spectra obtained on the outer surface of the Al-Mg-Si specimen after the etching process. These spectra are also representative of the Mg2p spectra observed on the Al-Cu and Al-Mg specimens. In contrast to the specimens after thermomechanical processing (Fig. 2a-2d), attention is drawn to the absence of magnesium on the surface of the etched specimens.

Figure 6 compares the Na1s high resolution XPS spectrum obtained on the outer surface of the Al-Mg specimen after thermomechanical treatment (Fig. 6a) with that obtained after the etching process (Fig. 6e). In contrast to the specimens after thermomechanical processing (Fig. 6a), attention is drawn to the presence of sodium.

3.4. Concentration profiles of the etched aluminium specimens

Figures 2-6 show the evolution with argon ion bombardment time of the high resolution spectra obtained on the surface of the etched alloys. The Al2p high resolution spectra for pure Al, Al-Cu, Al-Mg-Si and Al-Mg are presented in figure 5a-5p. The Mg 2p high resolution spectra for the etched Al-Mg-Si alloy is shown in figure 2e-2h; no appreciable Mg signal is obtained on the etched surface of this alloy.

Figure 3e-3h shows the Cu2p_{3/2} high resolution XPS spectra obtained on the surface of the etched Al-Cu alloy. The behaviour of the Al-Cu alloy contrasts with that for the above – mentioned Al-Mg-Si alloy. Now, on the surface of the etched Al-Cu alloy (but not on the surface after thermomechanical treatment) an important increase with AIB is detected in the intensity of the Cu signal, which belongs principally to metallic state (CuLMM Auger at 918 eV, not shown).

Figure 6e-6h shows the Na 1s high resolution XPS spectra obtained on the surface of the etched Al-Mg alloy after AIB. The NaKLL Auger peak is at 990.6 eV (not shown), which is very close to the value for Na⁺ (989.8 eV)

The detection of significant changes in the Cu and Na contents on the Al-Cu and Al-Mg alloys, respectively, with argon ion bombardment time suggests a stratum-type distribution of these elements. The Cu-rich stratum would be situated immediately below the metallic surface, while the Na-rich stratum would be situated in the oxide layer that covers the metallic surface.

The thickness of the aluminium oxide layer on the surface of the aluminium specimens was calculated using the expression given by Strohmeyer [10]:

$$d_o \text{ (nm)} = \lambda_{\text{oxide}} \sin \theta \ln [(I_{\text{oxide}} \times \lambda_{\text{metal}} \times N_m) / (I_{\text{metal}} \times \lambda_{\text{oxide}} \times N_o) + 1] \quad (1)$$

where: d_o is the thickness of the aluminium oxide layer (in nm); θ is the photoelectron output angle; I_{metal} and I_{oxide} are the intensities of the aluminium components in metallic state and as oxide from the Al2p peak (Figs. 5a-5p); λ_{metal} and λ_{oxide} are the mean free path of photoelectrons in the substrate and the oxide layer; and N_m and N_o are the volume densities of aluminium atoms in metal and oxide [17]. The fact that the intensity of the component associated to metallic aluminium (I_{metal}) is practically negligible on the unbombarded Al-Cu and Al-Mg alloy surfaces (Figs. 5b and 5d, respectively) implies a problem for the thickness determination of the surface oxide layers. For this reason, thickness values have also been calculated after 10, 20 and 30 minutes of AIB (Fig. 7), whose extrapolation to zero bombardment time provides more reliable estimations.

3.5. Analysis of the outer surface of aluminium alloys after the etching process and after 6 months' exposure to the laboratory atmosphere

No marked differences have been observed in the elemental composition obtained by XPS on the surfaces of the various aluminium specimens after etching and 6 months' exposure to the laboratory atmosphere compared with the original etched specimens (Table 3), and the results are therefore not shown.

The evolution with argon ion bombardment time of the Al2p high resolution XPS spectra obtained on the surface of the etched pure Al, Al-Cu, Al-Mg-Si and Al-Mg specimens exposed for 6 months to the laboratory atmosphere is presented in figures 8a-8l. The evolution with argon ion bombardment time of the Cu2p and Na1s high resolution XPS spectra obtained on the surface of the Al-Cu and Al-Mg specimens, respectively, were similar to those obtained on the original etched specimens (Figs. 3e-3h and Figs. 6e-6h) and are not shown.

Figure 7 (dotted line) shows the evolution of the residual oxide layer thickness on the etched aluminium substrates after different times of sputtering.

4. DISCUSSION

4.1. Composition of aluminium oxide overlayers on aluminium substrates after thermomechanical processing

Table 2, which has been obtained by XPS with the various aluminium specimens after thermomechanical processing, shows an important magnesium content on the outer surface of the Al-Cu, Al-Mg and Al-Mg-Si alloys in comparison with its absence on the pure Al surface. This result is in consonance with the presence of appreciable amounts of Mg in the bulk of these alloys, but not with the proportion of this element (Table 1), and seems to indicate a saturation of the outer aluminium surface with magnesium. According to the Mg/(Mg+Al) ratio in Table 2, the atomic percentage of the surface covered by Mg would be around 20%. This figure is similar to the results obtained by Lea and Ball [16] with annealed Al-Mg alloys containing 0.8% wt. and 2.5% wt. Mg; according to these authors, the oxide film formed on Al-Mg alloys at high temperatures soon becomes magnesium rich because the activation energy for diffusion is lower for magnesium than aluminium in both the metal and the oxide film [16].

The literature [1, 2, 8, 18-24] mentions a tendency for the formation of MgO overlayers during the annealing process of aluminium alloys with similar Mg contents to those used in this study. A similar tendency seems to be reflected in the results obtained in the present work shown in Fig. 2a-2d and Table 2.

Figure 1c reveals a very significant increase in the intensity of the metallic Al component and a reduction in the intensity of the Al³⁺ component in the Al2p high resolution XPS peak on the Al-Mg-Si specimen surface in comparison with the pure Al specimen (Fig. 1a). It seems likely that the increase in metallic Al is caused by the greater oxygen affinity of Mg, which could reduce the aluminium oxide content present on the outer surface during the solubilisation and artificial ageing of the Al-Mg-Si alloy. Goldstein and Dresner [18] studied the oxidation of pure Al-Mg alloys containing 0.1-3.0% Mg. They found that initial oxidation at room temperature gave alumina. Heating to 723 K led to the accumulation of magnesium in the alumina and some magnesium oxide was formed from the reaction:

Similar results have been described by Textor and Grauer [19] and Scotto-Sheriff et al. [20]. This reaction must be favoured by the high Mg content (Table 2) on the outer surface of the aluminium. Arouse attention the marked difference in the shape of the Al2p high resolution spectra for the Al-Mg-Si (Fig. 1c) and Al-Mg (Fig. 1d) alloys. In the latter the intensity of the metallic Al component is much lesser than that of the Al³⁺ component, which is the reverse of what observed with the Al-Mg-Si alloy. It seems as if the reduction reaction of the Al₂O₃ by Mg has not, or hardly occurred, presumably due to the great influence of the thermomechanical history on such a reaction. Thus, the observed difference in behaviour of the two alloys may be ascribed to the fact that Al-Mg-Si had been solution heat treated, whereas Al-Mg was strain-hardened only. Some published work [18, 20] have found a significant effect of heating treatment of the samples on the detection of metallic Al in naturally formed Al₂O₃ layers on aluminium alloys containing Mg.

Attention will be given to the ratio of the intensity of aluminium oxide component to the intensity of metallic aluminium component which is deduced from the Al2p high resolution peak. It can be seen that these ratios on the surface of the Al-Cu alloys (Figs. 1b, 1f, 1i and 1l) and the Al-Mg alloys (Figs. 1d, 1h, 1k and 1n) are higher than on the pure Al (Figs. 1a and 1e) and the Al-Mg-Si alloy (Figs. 1c, 1g, 1j and 1m). This is explained by accepting that the oxide film thickness on the Al-Cu and Al-Mg alloys after thermomechanical processing is greater than that observed on the pure Al and Al-Mg-Si alloys (Fig. 7).

4.2. Composition of aluminium oxide overlayers on aluminium substrates after the etching process

It should be noted that the important Mg content observed in the XPS analyses of the original surface of the Al-Cu, Al-Mg-Si and Al-Mg alloys (Table 2 and Figs. 2a-2d) disappears after the etching process. Table 3 shows that the only elements detected have been O, Al, and Na, the latter only in the case of the Al-Mg alloy. Similar results with regard to the disappearance of Mg from the outer surface of chemical or electrochemical treated aluminium alloys containing Mg

have been obtained by other investigators [6, 16, 21, 25, 26]. This behaviour contrasts with the results obtained with the same alloys after the thermomechanical processing on whose surfaces only Mg is detected (Table 2). Chemical cleaning treatments are believed to remove the Mg-enriched oxides above a more stable Al_2O_3 barrier layer [2]. The absence of MgO after the etching process suggests that this oxide was located mainly in the outermost layers of the aluminium alloys and it does not form at room temperature in the ambient atmosphere.

In the XPS analyses of the aluminium alloy surfaces after etching it is interesting to highlight the appearance of a significant Cu content in metallic state on the surface of the Al-Cu alloy after light argon ion bombardment (Figs. 3e-3h) and Na in ionic state on the surface of the Al-Mg alloy (Figs. 4 and 6e-6h). Also in regard to these two elements, the observed behaviour contrasts with that of the specimens after the thermomechanical processing (Figs. 3a-3d and 6a-6d).

According to the literature, chemical and electrochemical treatments of Al-Cu alloys can greatly increase the copper concentration close to their surface [27, 29]. The reason for this enrichment is that the dissolution of the alloy proceeds through an amorphous alumina-based film, so the metal atoms are oxidised at the alloy/film interface and migrate through the film before entering the solution. Due to the higher Gibbs free energy for copper oxide formation than for alumina formation, copper atoms in solid solution in the aluminium matrix cannot initially be oxidized leading to an increased copper concentration in the alloy, in a film thickness of up to ~2 nm [27, 30].

All the studied alloys contain small but significant sodium contents in their bulk (Table 1), so it is curious that the superficial presence of Na is revealed in only one of them (Al-Mg) (Fig. 4). It is also surprising that this phenomenon has appeared after the etching treatment and not on the thermomechanically processed surfaces. Werret et al. [1] found that traces of elemental sodium segregate to the surface during the oxidation of aluminium-silicon alloys. However, no such segregation has shown after thermomechanical processing in the alloys studied in this work,

possibly because the relatively coarse aluminium oxide and magnesium layer that coats the material may have prevented detection of the sodium signal.

Like the case of copper surface enrichment, the presence of sodium on the surface of the Al-Mg alloy may be attributed to the preferential dissolution of the aluminium in the alloy during etching [20,30]. The condition that sodium atoms must be in solid solution for the phenomenon of enrichment to occur provides an explanation to the difference in behaviour between this alloy and the other tested materials. In this respect, it seems likely that sodium in the Al-Mg-Si, Al-Cu and pure Al materials is retained forming part of the composition of precipitated second-phase particles, such as NaAlSi_x [31, 32], while in the Al-Mg alloy an important part of the Na remains dissolved in the matrix. The release of free sodium must be assisted by the higher Mg content in the latter alloy, which promotes the formation of the Mg_2Si phase, which is more stable than the NaAlSi compounds [31, 33].

On the other hand, the high oxygen affinity of sodium explains why it is found in ionic state on the surface of the Al-Mg alloy. The fact that a comparable ionisation of copper on the surface of the Al-Cu alloy has not been detected may be due to the more noble character of copper, which does not favour its ionisation.

The notably lower intensity of the metallic aluminium signal on the surface of the Al-Cu (Fig. 5b, 5f, 5j and 5n) and Al-Mg specimens (Fig. 5d, 5h, 5l and 5p), compared with the Al-Mg-Si (Fig. 5c, 5g, 5k and 5o) and pure Al specimens (Fig. 5a, 5e, 5i and 5n), is interpreted as being due to the greater thickness of the oxide films on the surface of the first two alloys. Results of film thickness calculations are compared in figure 7. The differences in film thickness among the various alloys are probably related with the degree of perfection of the oxide films and differences in diffusion rate [34, 35]. Thus, the greater thickness of the oxide layers on Al-Cu and Al-Mg would be caused by less compact films compared with those formed on the Al-Mg-Si and pure Al specimens. This behaviour seems reasonable considering, on the one hand, the tendency for the formation of defective films at the points on the Al-Cu alloy surface where precipitates of the Cu-rich phase emerge [7] and, on the other hand, the abundance of voids

close to the Al-Mg alloy film interface due to the significantly lower Pilling-Bedworth ratio for the formation of MgO compared with that of Al_2O_3 [36, 37].

4.3. Effect of atmospheric exposure on the oxide film thickness

In Fig. 7 it is interesting to note the increase in the aluminium oxide film thickness on the surface of the Al-Cu and Al-Mg alloys after 6 months of exposure compared with the absence of significant changes on the pure Al and Al-Mg-Si alloy, except for the not very reliable point corresponding to the outer surface of the latter alloy.

It is known [38] that natural oxide films on the aluminium can grow in thickness owing to the formation of aluminium hydroxide in a humid atmosphere when noble second-phase particles are present in the Al matrix; in this case the cathodic reaction (reduction of oxygen) occurs on the surface of these particles, while the anodic dissolution of aluminium is located in the surrounding matrix. This fact might explain the observed film increase in Fig. 7 in the case of the Al-Cu alloy, system in which most of the precipitated particles tend to behave cathodically [39]. Concerning the Al-Mg alloy, the faulty oxide film resulting from a Pilling-Bedworth ratio less than unity [36, 37] would facilitate diffusion processes, and enhance the susceptibility of the surface to corrosion in the presence of humid air. The presence of Na in the oxide film on the Al-Mg alloy suggests also another possible explanation based on the profound effect of alkaline elements on the surface reactivity (and corrosion resistance) of the samples exposed to humid air [19].

Comparison of Figs 6 and 8 indicates that the shape of the spectra for the various alloys scarcely has changed with exposure time. Similarly to the fresh etched specimens (Figs. 3e-3h and 6e-6h), the surfaces of the Al-Cu and Al-Mg alloys after 6 months of exposure show the presence of copper and sodium, respectively.

5. CONCLUSIONS

It has been verified that considerable changes take place in the chemical composition of aluminium oxide films on the four tested alloys (Al-Cu, Al-Mg, Al-Mg-Si and pure Al) as a

function of the alloying and depending on whether the film has formed during the thermomechanical treatment of the material or is the result of the subsequent etching process.

In particular, the following aspects are underlined:

- 1) On all the studied specimens it has been seen that after thermomechanical processing Mg is the alloying element with the greatest tendency to segregate towards the surface. With a Mg content of 0.8% wt. it has been found that close to 25% of the outer surface of the aluminium alloys is covered with Mg atoms. During the solubilisation process or the annealing of these alloys, metallic Mg diffuses towards the outer surface where it precipitates in the form of MgO, probably because of the reduction of aluminium oxide by Mg.
- 2) On the etched alloys it is interesting to note the appearance of a significant Cu content in metallic state close to the surface of the Al-Cu alloy, and Na in ionic state on the outer surface of the Al-Mg alloy, as well as the absence of Mg on the surface of the latter alloy. This result contrasts with the absence of these two elements on the surface of the same alloys and the presence of Mg after the thermomechanical processing.
- 3) Of the four tested materials, only Al-Mg shows Na-enrichment of its surface, despite the fact that this element is contained as an impurity in the bulk of all the alloys. It is suggested that this phenomenon may be linked to the presence of free sodium in the matrix, and not to the sodium retained in the form of second-phase particles.
- 4) After the etching process, a notably greater aluminium oxide overlayer thickness is determined on the surface of the Al-Cu and Al-Mg than on the Al-Mg-Si and pure Al specimens.

- 5) The utility of XPS analysis of aluminium surfaces for studying the characteristics of aluminium oxide films resulting from the thermomechanical processing and surface treatment of aluminium alloys has been verified.

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REFERENCES

1. C.R. Werrett, D.R. Pyke, A.K. Bhattacharya. *Surf. Interface Anal.* 25 (1997) 809-816.
2. C.E. Moffitt, D.M. Wieliczka, H.K. Yasuda. *Surf. Coat. Technol.* 137 (2001) 188-196.
3. A. Barbucci, G. Bruzzone, M. Delucchi, M. Panizza, G. Cerisola. *Intermetallics* 8 (2000) 305-312.
4. C.M.A. Brett. *Corros. Sci.* 33 (1992) 203-210.
5. G.S. Chen, M. Gao, R.R. Wei. *Corrosion* 52 (1996) 8-15.
6. O. Lunder, B. Olsen, K. Nisancioglu. *Int. J. Adhes Adhes.* 22 (2002) 143-150.
7. E. Huttunen-Saarivirta, T. Tianien. *Mater. Chem. Phys.* 85 (2004) 383-395.
8. D. Chidambaram, C.R. Clayton, G. P. Halada, N.W. Kendig. *J. Electrochem. Soc.* 151 (2004) B 605-B 612.
9. A. Roberts, D. Engelberg, Y. Liu, G.E. Thompson, M.R. Alexander. *Surf. Interface Anal.* 33 (2002) 687-703.
10. B.R. Strohmeier. *Surf. Interface. Anal.* 15 (1990), 51-56.
11. E.V. Koroleva, G.E. Thompson, G. Hollrigl, M. Bloeck. *Corros. Sci.* 41 (1999) 1475-1495.
12. J.A. González, V. López, E. Otero, S. Feliu, Jr, E. Escudero, M.J. Bartolomé, Project MAT2003-02217, "Effect of the size and concentration of intermetallic precipitates in the corrosion behaviour of anodized aluminium alloys".
13. K. Horikawa, S. Kuramoto, M. Kanno. *Acta Mater.* 49 (2001) 3981-3989.
14. C.D. Wagner, L.E. Davis, M.V. Zeller, J.A. Taylor, R.H. Raymond, L. Gale. *Surf. Interface Anal.* 3 (1981) 211-225.
15. J. Prokop, A. Kukunin, M. Pratzner, H.J. Elmer. *J. Magn. Magn. Mater.* 265 (2003) 60-68.
16. C. Lea, J. Ball. *Appl. Surf. Sci.* 17 (1984) 344-362.
17. C. Chen, S.J. Splinter, T. Do, N.S. McIntyre. *Surf. Sci.* 382 (1997) L652-L657.
18. B. Goldstein, J. Dresner. *Surf. Sci.* 71 (1978) 15-26.
19. M. Textor, R. Grauer. *Corros. Sci.* 23 (1983) 41-53.
20. S. Scotto-Sheriff, E. Darque-Ceretti, G. Plassart, M. Aucoutier. *J. Mater. Sci.* 34 (1999) 5081-5088.
21. A. Afseth, J.H. Nordlien, G.M. Scamaan, K. Nisancioglu. *Corros. Sci.* 43 (2001) 2359-2377.

22. G. Buytaert, H. Terryn, S. Van Gils, B. Kernig, B. Grzemba, M. Mertens. *Surf. Interface Anal.* 37 (2005) 534-543.
23. A. Raveh, Z.K. Tsameret, E. Grossman. *Surf. Coat. Technol.* 88 (1996) 103-111.
24. K.J. Holub, L.J. Matienzo. *Appl. Surf. Sci.* 9 (1981) 22-38.
25. T.B. Gundersen, A. Aytac, J.H. Nordlien, K. Nisancioglu. *Corros. Sci.* 46 (2004) 697-714.
26. H. Leth-Olsen, K. Nisancioglu. *Corros. Sci.* 40 (1998) 1179-1194.
27. X. Wu, K. Herbert. *J. Electrochem. Soc.* Vol. 143 No. 1 (1996) 83-91.
28. X. Zhou, G.E. Thompson, H. Habazaki, K. Shimizu, P. Skeldon, G.C. Wood. *Thin Solid Films* 293 (1997) 327-332.
29. Y. Liu, F. Colin, P. Skeldon, G.E. Thompson, X. Zhou, H. Habazaki, K. Shimizu. *Corros. Sci.* 45 (2003) 1539-1544.
30. C.E. Caicedo-Martinez, E. Koroleva, P. Skeldon, G.E. Thompson, G. Hollrigl, P. Bailey, T.C.Q. Noakes, H. Habazaki, K. Shimizu. *J. Electrochem. Soc.* 149 (2002) B139-B145.
31. D. Webster. *Metall. Trans.* 18 A (1987) 2181-2193.
32. L.F. Mondolfo in, *Aluminium Alloys: Structure and Properties*, Butterworths, London 1976, pp. 601-602.
33. C.E. Ransley, D.E. Talbot. *J. Inst. Met.* 88 (1959-60) 150-158.
34. C. Ocal, B. Basurco, S. Ferrer, *Surf. Sci.*, 157 (1985), 233-243.
35. N.A. Braaten, J.K. Grepstad, S. Raaen, *Surf. Sci.*, 222 (1989), 499-511.
36. X. Zhou, G.E. Thompson, P. Skeldon, G.C. Wood, K. Shimizu, H. Habazaki. *Corros. Sci.* 41 (1999) 1599-1613.
37. Y. Liu, P. Skeldon, G.E. Thompson, X. Zhou, H. Habazaki, K. Shimizu. *Corros. Sci.* 43 (2001), 2349-2357.
38. I. Olefjord, A. Nylund. *Surf. Interface Anal.* 21 (1994) 290-297.
39. R.P. Wei, Chi-Min Liao, M. Gao. *Metall. Mater. Trans. A*, 29A (1998), 1153-1160.

TABLES

Table 1. Chemical composition of aluminium alloys (weight percentages).

DESIGNATION	ALLOY	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Na
Pure Al	1050	0.080	0.290	0.003	0.003	0.006	...	0.040	0.012	0.020
Al-Cu	2017	0.370	0.340	4.040	0.630	0.600	0.010	0.050	0.050	0.020
Al-Mg-Si	6082	0.880	0.360	0.040	0.470	0.800	0.003	0.040	0.060	0.030
Al-Mg	5754	0.090	0.260	0.001	0.110	2.900	...	0.022	0.004	0.040

Table 2. Atomic percentages observed by XPS on the outer surface of the aluminium alloys after thermomechanical processing.

SPECIMEN	% O	% Al	% Mg	% Mg/(%Mg+%Al)
Pure Al	65	35	0	0
Al-Cu	45	45	10	0.18
Al-Mg-Si	36	48	16	0.25
Al-Mg	52	38	10	0.20

Table 3. Atomic percentages observed by XPS on the outer surface of the aluminium alloys after the etching process.

SPECIMEN	% O	% Al	% Na
Pure Al	67	33	0
Al-Cu	72	28	0
Al-Mg-Si	76	24	0
Al-Mg	74	25	1

FIGURE CAPTIONS

Figure 1. Evolution with AIB time of Al2p high resolution XPS spectra for pure Al, Al-Cu, Al-Mg-Si and Al-Mg specimens after thermomechanical processing.

Figure 2. Comparison of the evolution with AIB time of Mg2p high resolution XPS spectra obtained on the Al-Mg-Si sample surface after thermomechanical processing and after etching.

Figure 3. Comparison of the evolution with AIB time of Cu2p_{3/2} high resolution XPS spectra obtained on the Al-Cu specimen surface after thermomechanical treatment and after etching.

Figure 4. Comparison of the general XPS spectra obtained on the pure Al, Al-Cu, Al-Mg-Si and Al-Mg alloy surfaces after etching.

Figure 5. Evolution with AIB time of Al2p high resolution XPS spectra obtained on the pure Al, Al-Cu, Al-Mg-Si and Al-Mg alloy surfaces after etching.

Figure 6. Comparison of the evolution with AIB time of Na1s high resolution XPS spectra obtained on the Al-Mg alloy surface after thermomechanical processing and after etching.

Figure 7. Comparison of the evolution of aluminium oxide film thicknesses on the etched specimens (continuous line) and after 6 months in the laboratory atmosphere (dotted line).

Figure 8. Evolution with AIB time of Al2p high resolution XPS spectra obtained on the pure Al, Al-Cu, Al-Mg-Si and Al-Mg alloy surfaces after etching and 6 months' exposure to the laboratory atmosphere.

Figura 1.

Figura 2.

Figura 3.

Figura 4

Figura 5

Al-Mg

Figura 6

Figura 7

Figura 8-