SODIUM ENRICHMENT OF AN Al-Mg ALLOY SURFACE AFTER ALKALINE ETCHING

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ABSTRACT

This paper reports a case of sodium enrichment of the surface of an Al-Mg alloy that contains sodium impurities in its bulk and has been subjected to etching treatment in an alkaline solution. This phenomenon has only occurred in the case of the aforementioned Al-Mg alloy and has not been observed in other tested Al-Cu, Al-Mg-Si or pure Al type alloys, despite the fact that these also contain sodium as an impurity. The origin of the sodium ions incorporated in the aluminium oxide film that covers the surface of the Al-Mg alloy is discussed, and an explanation is suggested for this difference in behaviour compared with the other alloys.

Keywords: Aluminium, oxide films, sodium enrichment, alkaline etching.

INTRODUCTION

Many papers have reported alloying element enrichment phenomena at or near the surface of aluminium alloys subjected to electrochemical or chemical treatments [1-9]. Alloying element atoms often accumulate in a layer immediately below the metal/oxide film interface, and from here can be incorporated in ionic form in the oxide film [1,4-10]. Although phenomena of this nature have been reported with a large number of alloying elements and impurities in aluminium, no references have been found to superficial sodium enrichment as a consequence of dissolution processes.

This communication reports a case of sodium enrichment of the surface of an Al-Mg alloy that contains sodium as an impurity, after being subjected to alkaline etching in a sodium hydroxide solution. This result has been obtained within a broader study of aluminium anodisation and surface treatments [11]. Curiously, other aluminium alloys that also contain sodium as an impurity have not shown a similar phenomenon.

EXPERIMENTAL

Materials tested

The study considers the following alloys: 1050, 2017, 5754 and 6082, whose compositions, determined in wet conditions, are shown in Table 1. The 1050 alloy is a commercially pure alloy (99.5%), and is henceforth referred to as pure Al; the binary alloys 2017 and 5754, with approximately 4% wt. Cu and 3% wt. Mg, are referred to throughout the work as Al-Cu and Al-Mg, respectively; and the ternary alloy with 0.9% wt. Si and 0.8% wt. Mg is designated as Al-Mg-Si. The relatively high sodium impurity contents may be associated with contamination introduced in the alloys via the aluminium and magnesium [12] used in the melting and casting process. Temper conditions and properties of the alloys employed are given in Table 2. The 1050 alloy was strain hardened. 2017 and 6082 alloys were solution heat treated and quenched to room temperature; the 2017 alloy was naturally aged and the 6082 alloy was aged at about 180°C. The 5754 alloy was batch annealed and cold rolled.

Surface preparation and alkaline etching

Individual specimens of 100 x 50 x 1.5 mm were degreased in acetone, followed by rinsing in water and immersion in an aqueous solution of 15% vol. phosphoric acid and 5% wt. chromic acid for 5 min at 30-40°C. They were then washed with distillate water and dried with a hot air stream.

The specimens were subsequently immersed in an aqueous solution of 10% wt. sodium hydroxide at 40°C for variable times and neutralised by immersion for several seconds in the aforementioned phosphochromic solution. Finally they were washed with distillate water and dried.

Alkaline etching removed between 8-15 μm of the alloy during the 5 min treatment time, depending on the degree of attack of each alloy type. All the experiments were repeated at least three times.

XPS study

Photoelectron spectra were recorded using a Fisons MT500 spectrometer equipped with a hemispherical electron analyser (CLAM2) and a Mg K α X-ray source operated at 300 W. The specimens were mechanically fixed on small flat discs supported by 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, accurate binding energies (BE) could be determined by referencing to the adventitious C1s peak at 285.0 eV. Atomic ratios were computed from peak intensity ratios and reported atomic sensitivity factors [13] The O1s high resolution spectra acquired on the surfaces were broad and featureless and no attempt was made to computer-fit these spectra. The Al2p envelopes exhibited one peak associated with oxidised Al.

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 into 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 specimen current was 1 μ A during bombardment [14]. In these conditions and with the spectrometer used in the study a sputtering rate of the order of 1-2 Å/min may be estimated [15, 16].

The XPS analyses were normally repeated two or three times, verifying reasonable reproducibility.

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

Figure 1 shows the general XPS spectra obtained on the outer surface of the various aluminium alloys after etching. Attention is drawn to the presence of Na on the surface of the Al-Mg alloy. Table 3 shows the element composition obtained by XPS on these surfaces. The sodium content reaches a value close to 1% at.

Figures 2a-2d show Na1s high resolution XPS spectra obtained on the surface of the etched Al-Mg alloy after AIB. The spectra obtained are fairly similar, presenting one single component with a binding energy of 1071.6 eV. The Na KLL Auger peak is at 990.6 eV kinetic energy (not shown), which is very close to the value for Na^+ (989.8 eV) and at some distance from the value for Na^0 (994.3 eV), for which reason the sodium present must mainly be in ionic form. An increase in the sodium signal intensity is observed after 10 minutes of AIB (Fig. 2b). Longer AIB times produce a decrease in intensity (Figs. 2c and 2d).

Oxide film thickness

The thickness of the aluminium oxide layer on the surface of the aluminium specimens was calculated using the expression given by Strohmeyer [17]:

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

where d_o is the thickness of the aluminium oxide layer (in nm); θ is the photoelectron output angle and I_o and I_m are the intensities of the aluminium components of the Al2p peak as oxide and in metallic state, 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 [18]. The fact that the intensity of the component associated to metallic aluminium (I_m) is practically negligible on the surface of the Al-Cu and Al-Mg alloys prior to bombardment 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 min of AIB, whose extrapolation provides the estimations with greater certainty. According to figure 3, oxide films of a thickness of between 2 and 4 nm normally coat the outer surface of the aluminium alloys after alkaline etching.

DISCUSSION

Enrichment by chemical dissolution

As to the origin of superficial sodium enrichment, one possibility is that Na species from the NaOH bath may have been incorporated in the hydroxide/oxide film that coats the surface during chemical attack. The fact that superficial sodium enrichment has only been detected on the Al-Mg alloy and not on the pure Al, Al-Cu or Al-Mg-Si alloys, which were also exposed to the Na^+ ions of the alkaline bath, clearly suggests that this is not the origin of this phenomenon (Fig. 1). Since long AIB times are insufficient to remove the sodium signal from the XPS spectrum of the Al-Mg surface (Fig. 2), the sodium must be deeply incorporated in the hydroxide/oxide film. This situation is typical of processes in which the incorporated element participates in the formation of the film, therefore the superficial sodium enrichment observed on the Al-Mg alloy must have been produced from the sodium contained as an impurity in the bulk alloy (Table 1). From Figure 2, the higher sodium signal intensity observed in Figure 2b suggests that the section analysed after 10 min. of sputtering may

represent the most favourable combination of sodium concentration and rate of transport of oxygen through the oxide layer.

According to the literature, the alkaline etching of aluminium takes place through an aluminium oxide/hydroxide film on the metal surface, with ionic migration through this film and the ejection of cations into the etching solution on reaching the film/solution interface [1,5-8,19-21]. The verified non-influence of rotation speed upon the reaction kinetics has been explained as being due to the fact that the aluminium surface is covered by a protective oxide/hydroxide film, which is dissolution rate-limiting [20,22,23]. The high Tafel slopes measured during alkaline etching are also consistent with the presence of an oxide/hydroxide film on the aluminium surface. The exact nature of this film is not known, although it is likely to be fundamentally of $\text{Al}(\text{OH})_3$ passivating species [23], whose solubility depends on their conversion into aluminates. The high interface capacitance values determined by EIS indicate that this is a very thin film, of some 2-3 monolayers in a 1M NaOH solution [21]. This film is therefore much thinner than the oxide films of a few nanometres thickness that normally coat the surface of aluminium in contact with atmospheric oxygen.

As different authors have shown, during chemical and electrochemical treatments of aluminium a thin layer of the metal immediately below the oxide/hydroxide film on the alloy surface may become enriched in alloying elements and impurities [1-9]. This enrichment occurs for those elements whose relative Gibbs free energy per equivalent ($\Delta G_0/n$) for the formation of the oxide is more positive than that for Al_2O_3 [8,9]. Once critical amounts of particular element atoms have been accumulated in the aforementioned thin metal layer, then these atoms can be oxidised and their ions incorporated in the aluminium oxide/hydroxide film. From that moment, the enrichment remains practically constant with time.

From data in the literature [24, 25], a value of -188 kJ for $\Delta G_0/n$ at 25°C is deduced for Na_2O formation per equivalent, whereas this value for Al_2O_3 is -263 kJ. As the free energy of oxide formation of Na is less negative than that for Al, the oxygen will show a preference for this last metal

and, on the basis of the $\Delta G_0/n$ criterion, sodium enrichment may be anticipated. Thus the sodium concentration in the metal just below the oxide/hydroxide film will grow in line with the metal thickness removed by the etching treatment unless it reaches the critical concentration necessary for the sodium atoms to oxidise and become incorporated in the oxide/hydroxide film. This process will be favoured by the lower energy of the Na-O bond than the Al^{3+} -O bond [4,8,26].

Considering that the amount of metal removed during 5 min. etching of the alloys has been 2-4 mg/cm^2 , and accepting the suppositions of (i) an enrichment layer of 2 nm thickness close to the alloy/solution interface, (ii) that all the Na atoms are retained in this thin metallic layer as the surrounding Al and alloying atoms dissolve, and (iii) that the free sodium concentration in the bulk alloy is 0.002% wt. (see below), a rough estimate indicates the possibility of enrichment of the order of 8-15% wt. Na. It is not known if this level of enrichment is sufficient for sodium to be oxidised during alkaline etching, as seems to suggest the detection of Na^+ ions by XPS analysis.

Location of sodium atoms

In order to understand the behaviour of alloying elements and impurities during aluminium surface treatments, a factor of considerable relevance is their location, particularly whether they are in solid solution or in second phases in the metal structure. The maximum solid solubility of sodium in aluminium has been reported to be of the order of 0.0020% wt. [27]. Therefore the Al-Mg alloy, which contains 0.004% wt. Na (Table 1), may have at most close to half of this sodium in the form of free atoms for the superficial enrichment detected in this work.

In the other tested materials, i.e. Al-Cu, Al-Mg-Si and pure Al, the absence of significant sodium enrichment suggests that practically all of this element is not located in solid solution but is present as sodium-rich particulates. Sodium is known to exist in most aluminium alloys as a compound of Al, Si and Na, with a formula between $(\text{NaAl})\text{Si}_2$ and NaSi_4Al [28,29]. In these conditions a relevant oxide/hydroxide film is not anticipated over the particles protruding from the surface during chemical

attack, and neither is the aforementioned enrichment phenomenon, at least to a significant extent, as the experimental results seem to show.

It has been noted [28,30] that ternary AlNaSi compounds do not form in the presence of a substantial amount of an element that forms a more stable silicide, as is the case of Mg in alloys containing more than 2% wt. Mg [28]. For this reason the tested Al-Mg alloy, which contains 3% wt. Mg, will have free sodium available for the enrichment mechanism, while in the other tested alloys, with Mg contents of less than 1% wt. (Table 1), the NaAlSi compounds must be stable and no free sodium will be present.

Ionisation of sodium

According to the enrichment theory, sodium may have been incorporated in ionic form in the aluminium oxide/hydroxide film from the enriched metal layer after reaching a certain critical enrichment level. It is not known to what extent this phenomenon is responsible for the amount of Na^+ ions detected in this work on the Al-Mg alloy surface after chemical attack, since there is also a possibility of the ionisation of sodium after the chemical attack. According to Emregül and Aksüt [21] an extremely thin oxide/hydroxide film (just a few monolayers thick) covers the aluminium surface during alkaline etching. The enormous difference between the thickness of this film and that determined a few days after etching (some 2-4 nm in thickness) (Fig. 3) suggests that most of the latter thickness has been built in the subsequent atmospheric exposure of the specimens after being removed from the bath. In this case the Na^+ ions determined by XPS would mainly come from the reaction of the sodium atoms concentrated in the enriched layer close to the alloy surface with the atmospheric oxygen.

CONCLUSIONS

XPS analysis has revealed considerable superficial sodium species enrichment of an Al-Mg alloy that has been chemically attacked in an alkaline solution. Curiously, this phenomenon has not been detected in other alloys such as Al-Cu, Al-Mg-Si or commercial purity Al subjected to identical

treatment and which, like the Al-Mg alloy, contain small amounts of sodium as an impurity in the bulk alloy.

In the enrichment phenomenon it is supposed that free sodium atoms present in the bulk of the Al-Mg alloy are retained in a very thin metal layer close to the alloy surface as the surrounding Al and other alloying atoms dissolve. The absence of significant sodium enrichment in the Al-Cu, Al-Mg-Si and pure Al specimens suggests that most of the sodium in these alloys is not located in solid solution but forms part of the composition of second-phase particles.

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FIGURE CAPTIONS

Figure 1. Comparison of general XPS spectra obtained on pure Al, Al-Cu, Al-Mg-Si and Al-Mg surfaces after etching.

Figure 2. Comparison of the evolution with argon ion bombardment time of Na1s high resolution XPS spectra obtained on the Al-Mg specimen surface after thermomechanical treatment and after the etching process.

Figure 3. Thickness of the aluminium oxide layer on the surface of the etched specimens.

TABLES

Table 1. Chemical composition of the 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. Type of alloy investigated and temper conditions (Aluminium Association (USA) designation).

Alloy	Temper	0.2% stress N/mm ²	Proof Tensile N/mm ²	Strength elongation %	Hardness HB
1050A	H14/H24	130	131	7	33
6082	T6/T651	290	327	14	94
5754	O/H111	120	224	23	52
2017A	T4/T451	303	413	15	110

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

SPECIMEN	% O	% Al	% Na	%Mg	%Cu	%Mn	%Si
Pure Al	67.3 $\pm$ 3.7	33.5 $\pm$ 3.7	0	0	0	0	0
Al-Cu	72.4 $\pm$ 1.8	28.7 $\pm$ 4.8	0	0	0	0	0
Al-Mg-Si	76.1 $\pm$ 0.5	24.6 $\pm$ 0.5	0	0	0	0	0
Al-Mg	74.7 $\pm$ 0.6	25.1 $\pm$ 2.0	0.89 $\pm$ 0.05	0	0	0	0

Figura 1.

Na 1s peak

Figura 2.

Figura 3.