

X-RAY PHOTOELECTRON SPECTROSCOPY ANALYSIS OF OXIDE FORMATION ON 8150 ALUMINIUM FOILS

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ABSTRACT

It is known that an enrichment of metallic elements in the oxide layer of aluminium foils may significantly affect their surface properties. Elemental compositions at various depths of the newly developed 8150 aluminium foil were determined by x-ray photoelectron spectroscopy for selected heat treatment conditions.

1. INTRODUCTION

In recent years there has been an increasing demand in the aluminium industry for the production of ultra-light gauge aluminium foil. To deform the metal into a light gauge, the aluminium alloy must maintain high ductility and formability during the rolling process. The 1xxx aluminium alloys series are commonly used in manufacture of aluminium thin foils. These alloys contain additions of silicon and iron in approximate amounts of 0.04% - 0.15% and 0.35% - 0.50% respectively, have a ductility of 35 - 40% and a moderate tensile strength of 75 - 90 MPa [1,2]. To develop the ultra-thin foils, several alloys have been investigated with the aim to obtain higher strength but without significant loss of ductility. A new alloy, designated as AA8150, which contains higher contents of silicon, iron and manganese, was recently developed at ALCOA-ARP [3]. With additions of iron and manganese, a fine dispersion of (FeMn)Al₆ dispersoids is expected to provide high strength to the alloy. An increased strength will allow the foils to be processed with less risk of a web break and enable lower gauges without a decrease in strength for various applications. The alloy therefore shows great advantages over the conventional 1xxx alloys for manufacture of ultra-light foils.

Aluminium foils are generally manufactured via thermomechanical processing with scheduled hot rolling, cold rolling and thermal heat treatments. During the thermal heat treatments and/or deformation processes, an oxide film forms on the surface of the foils. Surface enrichment of metallic elements may occur in the oxide layer, and modify the properties of the oxide film and influence the surface of the aluminium foils. It has been reported that at a temperature as low as 260°C, some metallic elements such as magnesium, lithium and sodium may readily migrate to the oxide surface of the aluminium foils [4-5]. An enrichment of magnesium in the oxide layer shows a deleterious effect on the properties of the foils, creating an enhanced susceptibility to surface corrosion and weakens the heat-seal adherence of the foils [6-7]. With the high contents of silicon, iron and manganese

in the 8150 aluminium alloy, it is therefore important to investigate the effects of these metallic elements on the oxide formation of the foils. This paper reports results obtained from a detailed study of the oxide formation on the 8150 foils at selected heat treatment conditions. The elemental compositions at various depths of the foils were determined using x-ray photoelectron spectroscopy (XPS) technique, and their related properties were examined and analysed.

2. EXPERIMENTAL PROCEDURES

A cast block of AA8150 aluminium alloy was rolled to a final thickness of 12 µm using a standard rolling schedule. Annealing heat treatments, which simulated approximate commercial boundaries for foil products, were applied. The first foil (B1) was annealed at 235°C for 72 hours and the second one (B2) was annealed at 285°C for 2 hours.

Composition measurement and depth profiling of the foils were conducted using ion bombardment and x-ray photoelectron spectroscopy (XPS) analysis on both the shiny and matte surfaces of the samples. General wide surface scans were conducted using a VG ESCALAB 220i XL-Ray with Al-Kα monochromatic x-rays. Depth profiles for both the shiny and matte surfaces of samples B1 and B2 were conducted using a VG ESCALAB 220i XL-Ray. Several foil specimens were cut to size and layers of the foils were separated for testing. The adjacent shiny and matte areas were profiled, with B1 assessed first. The process involves Argon ion bombardment over a specified area at a rate of 2 angstroms per sec for a period of 12.1 seconds forty times to a depth of 50nm. For the B2 samples this was reduced to a depth of less than 20nm, with the matte side sample of B2 run for 14.2 seconds. The samples were not washed or cleaned prior to analysis.

3. RESULTS AND DISCUSSION

X-ray photoelectron spectroscopy analysis was conducted on both the shiny and matt surfaces of the 12 µm foils after heat treatments of 285°C for 2 hours

and 235°C for 72 hours respectively. General wide surface scans, for example, Figure 1, show that surface of shiny and matte surfaces for both samples are composed of oxygen, aluminium and carbon species, along with trace elements manganese, magnesium, tin, copper, fluorine and nitrogen. Wide survey scans provide only a general idea of surface characteristics, with all samples examined in the context of this study having similar spectra.

Thus, the general wide surface scans gave little information other than identifying the presence of oxygen, aluminium and carbon, as well as several trace elements. Results from the general wide survey scans for surface oxide and contaminants are summarized in Table 1. The scan shows a double peak with the presence of hydroxides, while the aluminium scan showed two distinct peaks, the lower one for aluminium metal, and the higher one for aluminium oxide, in the form Al_2O_3

High resolution scans were made on the elemental compounds detected to allow a closer examination of the contaminants, particularly carbon and oxygen as well as the aluminium.

The carbon scans (Figure 2) show a double peak, as well as some peak width spread in both peaks. The double peak indicated the presence of carbonaceous material, probably composed of CH_n groups as well as a small amount of oxidised carbon functional groups. Oxidised carbon groups occur at a slightly higher binding energy than the hydrocarbon group (287-290eV versus 286eV) due to the difference in electronic environment of each atom, and were found to be organic hydroxyls and carboxyls. All elements detected are curve fitted in accordance with a known organic sample. The carbon spectra showed three peaks for all samples with the larger peak at 286.1 – 286.4eV would be assumed to be a slightly shifted ($\approx 2eV$) hydrocarbon group. The charging shift is associated with insulating materials [8]. The broad base was found to be due to the presence of alkoxy groups in the form of organic hydroxyls that would occur at a shifted value of 287.7-287.8eV. The third peak consisted of an oxidised carbon functional group in the form of carboxylic acids at 290.2-6eV. XPS analysis of the thin film surface showed the presence of carbonaceous surface contaminants along with various oxides and alkali and alkali earth metals.

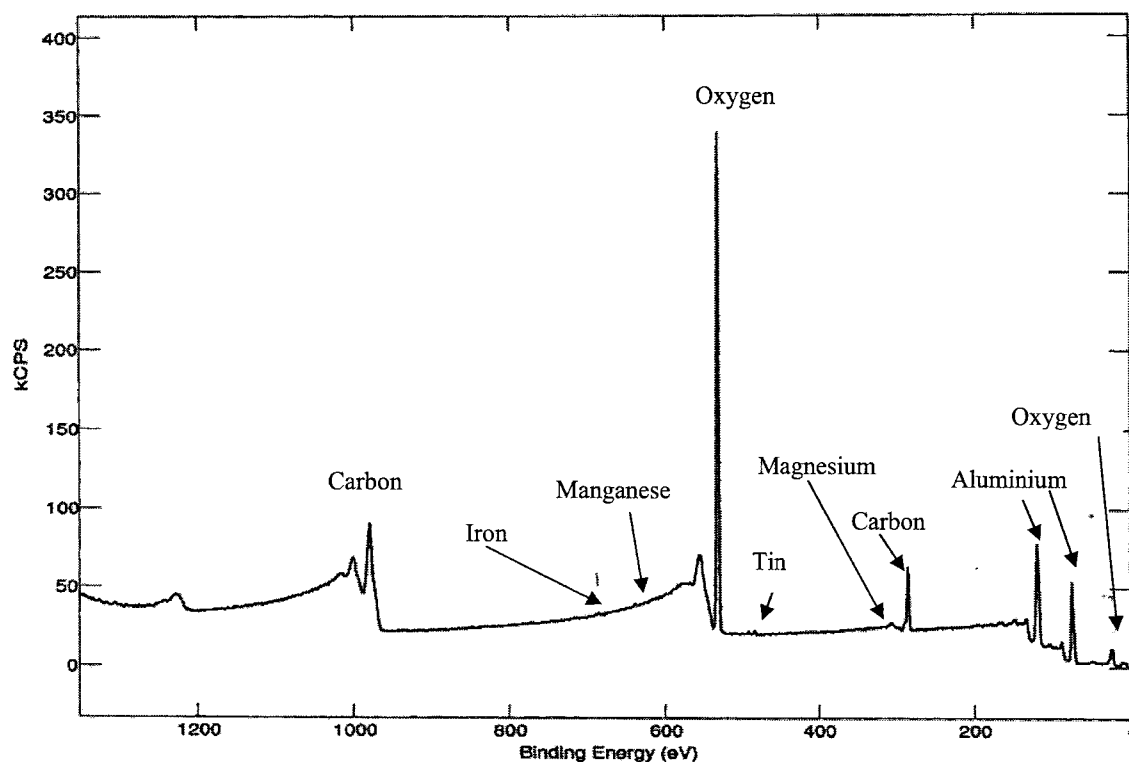


Figure 1: XPS wide surface scan for shiny side of aluminium foil

Table 1: Summary of XPS Quantification (at. %)

Sample	B1		B2	
	Shiny 235°C	Matte 235°C	Shiny 285°C	Matte 285°C
Al – Oxide	27.23	26.43	28.25	28.85
Al – metal	6.58	7.34	7.01	8.8
O – Al oxide	24.51	24.55	17.87	28.11
O – Al hydroxide	15.03	13.46	20.48	14.60
O – Other	6.57	7.61	7.61	5.66
C – Hydrocarbon	16.6	16.05	16.03	11.45
C – Org Hydroxyl	1.34	1.70	0.81	0.93
C – Carboxyl	2.02	2.33	1.75	1.38
Sn – Oxide			0.02	0.01
Sn – Metal			0.03	0.05
Mn – Oxide	0.02	0.02	0.02	0.02
Mn – Metal	0.04	0.04	0.03	0.04
Mg – Oxide		0.15	0.10	
Cu – Oxide	0.05	0.05		
F				0.10
N		0.28		

The carbonaceous residues were found to be composed mainly of hydrocarbons, with traces of organic hydroxyls and carboxylic acids an order of magnitude less. There is a small increase in binding energy and base spread for carbon based products as the annealing temperature increased, but time decreased. At temperatures below 250°C, the B1 samples in this work, oxidation rather than polymerisation occurs. At temperatures of around 300°C, the B2 sample here, some polymerisation occurs although oxidation predominates [9]. This indicated that for temperatures below 300°C where oxides start to crystallize, the heating process time is critical in controlling oxidation and polymerisation.

An examination of the shiny and matte sides showed no practical difference in total oxygen or carbon levels, with one matte sample having a much lower surface hydrocarbon contamination, believed related to the

application technique rather than reaction kinetics. While William's work [9] suggested that residual lubricant polymerization is the main mechanisms for stickiness, there is still a train of thought that surface oxidation of the residual lubricant and aluminium interface are factors. These observations are consistent with William's observations of non-sticky foil, with lubricant polymerisation the main mechanism for stickiness. This will also aid in controlling streaky matte defects. It also increases the annealing scope for thin film alloys, supporting higher annealing temperatures (up to 300°C max.) while reducing annealing times without significantly affecting unwindability of a coil. The ratio of time to temperature still requires further investigation, with heat-up and cools down rates to remain constant.

High resolution scans (Figure 3) for oxygen showed a broad single oxygen peak that was due to the presence of both aluminium oxide and aluminium hydroxides at 533.1eV and 532.1eV respectively, as well as a smaller peak at 533.9eV which further supports the presence of alkoxygroups

The presence of hydroxides at the surface indicate either humid slitting and/or annealing conditions, or the production of water from the chemical reactions during annealing bonding with the aluminium metal surface to produce aluminium hydroxides. While the atomic % values were proportionally high, work by Williams indicated that they had a negligible effect on stickiness. As all samples unwound easily with no addition force, this observation is supported

Depth profiles (for example, see Figure 4) obtained using ion bombardment and XPS analysis revealed a slight increase in aluminium oxide at the surface with a corresponding drop in 'other' oxides to about the 0.3-0.5nm mark. This corresponds with William's observations that the carbonaceous residue appears to be approximately 0.3nm thick. Both oxides then follow an inverse logarithmic growth pattern until a depth of between 5 to 15nm, where the oxygen diffusion layer starts for a further 10-20nm. It appeared that the 'other' oxides also diffused in the metal surface at a similar rate to that of aluminium hydroxide. The exact transition point is difficult to establish as there no recognized international guidelines on measuring oxide thickness using XPS data.

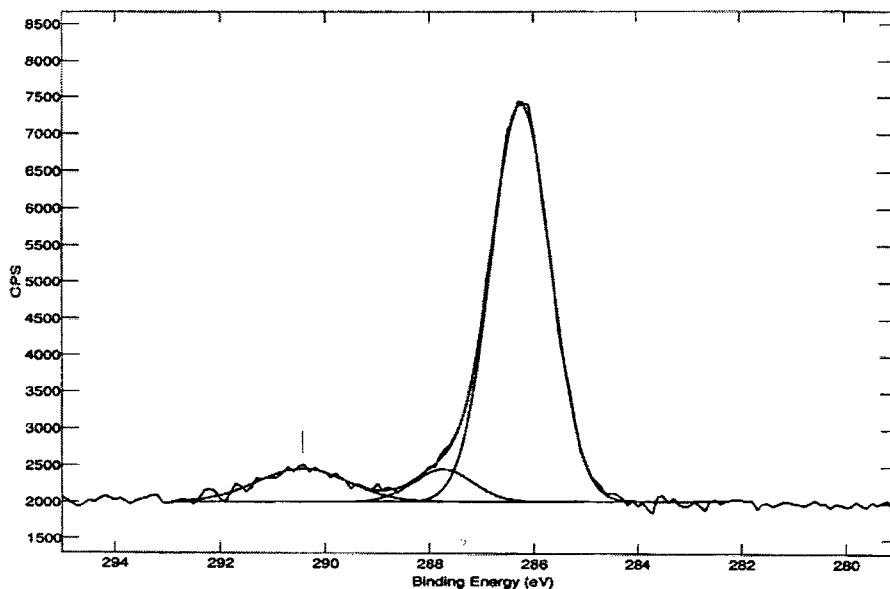


Figure 2: High resolution XPS scan - carbon region

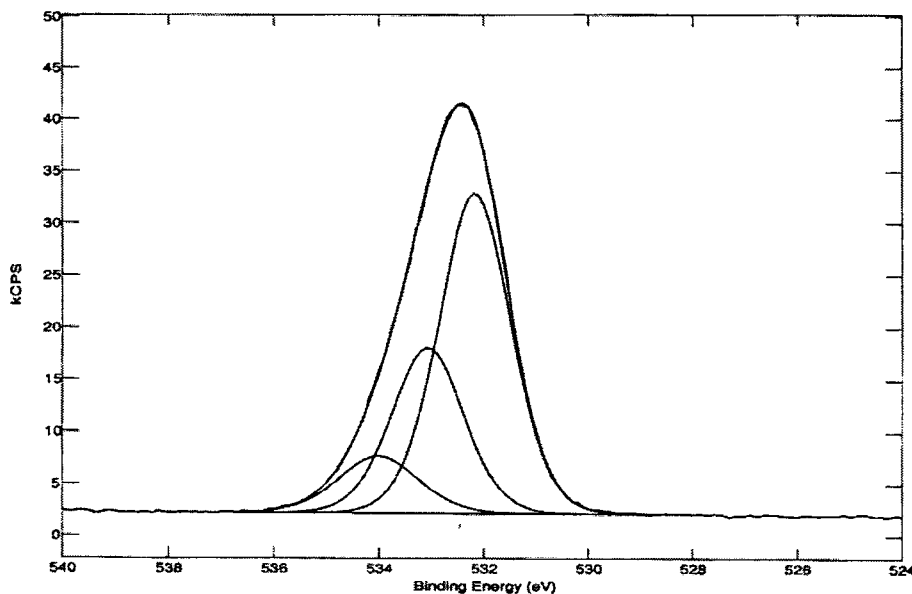


Figure 3: High resolution XPS scan - oxygen region

The presence of trace elements such as fluorine, nitrogen and tin are a thought to be contaminants from either the natural gas supply that is used to fire the furnaces, or in the case of tin, impurities in the coolant from gear-oil and other heavy oil leaks. Some manganese was expected, present in oxide and metal trace amounts. This may be related to either the alloy or bearing greases from processing.

The presence of copper and magnesium was anticipated, as furnaces used to cast these alloys also cast high copper and magnesium alloyed products. These two alloys, along with manganese, leach into refractory bricks, and can contaminate purity alloys such as 1xxx and 8xxx series alloys if not 'washed out'

correctly. Both alloy additions are not unheard of in 8xxx series alloys, with ALCAN having a patent on the addition of it to alloy 8006, itself a patented alloy [10,11,12]

Copper promotes a finer grain structure, increasing burst strength but also increasing the corrosion susceptibility of the metal, particular when used in frozen food applications. Magnesium is detrimental on laminated product, as MgO 'islands' can reduce the adhesions at the lamination boundary [13.] The presence of these elements must be kept at low levels.

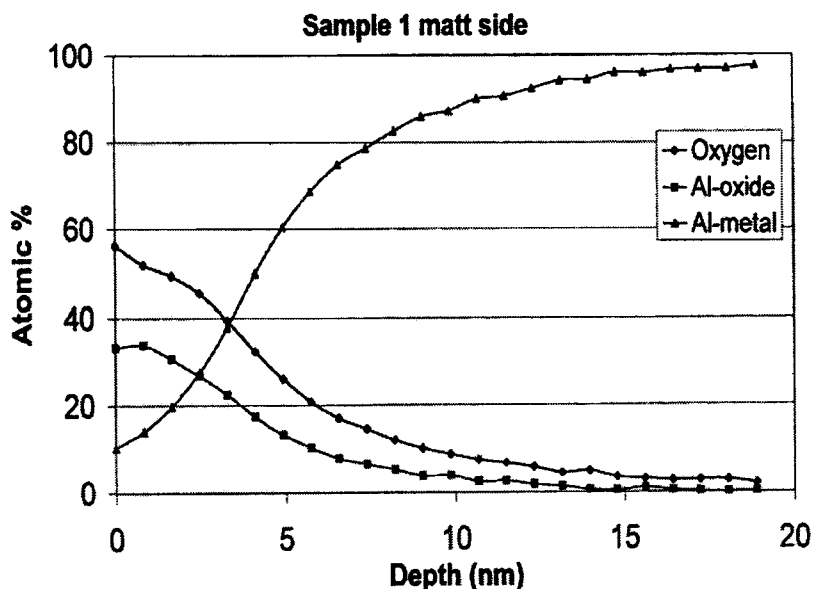


Figure 4: XPS depth profile

4. CONCLUSIONS

XPS was used successfully to investigate the surface of rolled aluminium foil. It was found that the surface composition was not affected significantly by the heat treatment schedules used in this work. It was also found that compositional differences between the shiny and matte sides of the foil were minimal.

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