



Oxide Growth on Aluminium Alloys in the Presence of Ammonium Fluoborate

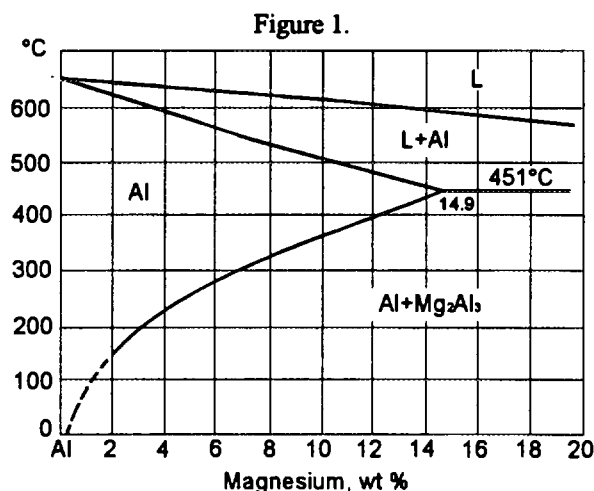
JAMES OLIVER & PETER PATERSON, Applied Physics Dept. RMIT
TERRY FLAVELL, Metallurgical Engineering Dept., RMIT
GERRY BIDDLE, Alcoa Rolled Products, Aust.

1. INTRODUCTION

The issues of oxide growth on rolled aluminium alloys, are a problem prior to rolling. Rolling requires that an ingot be heated to temperatures above 500°C, and held for periods greater than four hours, which allows substantial oxide growth, as well as chemically and mechanically driven diffusion of some elements to the surface.

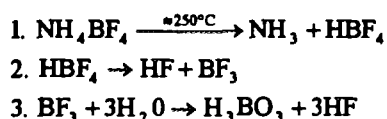
In the ammonium fluoborate has been used to control oxide growth during preheating. Their current published literature suggests however that the mechanisms involved with the usage of this chemical are unknown for AA5182. It was the aim of this study to determine the mechanisms involved in using ammonium fluoborate as a reducing atmosphere when preheating a high magnesium content aluminium alloy. The preheated alloy was compared for both air and ammonium fluoborate atmospheres.

A cast 5182 alloy comprises of approximately 4.5 wt% magnesium, lesser amounts of manganese, iron, silicon, copper and chrome (>1.5 wt%), as well as trace amounts of a number of other elements including gallium, zinc, titanium and vanadium. These elements, along with the industrial processing operation, are cause for a multitude of compounds to form, such as salts and intermetallics. It is known that the inclusion of compounds in an alloy will affect its cast structure and melting point. This is also evident as being chemically driven, by the readiness of magnesium and oxygen bonding to form Mg_2O . Saied and Sullivan (1) established that Mg is chemically driven to the surface of aluminium to react with excess oxygen. The Al-Mg phase diagram (2), figure 1, clearly shows the solidus line below 600°C at 4.5% magnesium, and allowing consideration for other impurities reducing the solidus line further, this feature could lower the melting point dangerously close to the typical homogenising temperatures.



Such temperatures as used, can enter the mushy zone of the material, and the consequential diffusion of magnesium occurs rapidly.

In 1989 Strohmeier (3) proposed the following equations as reactions involved with the use of ammonium fluoborate;



These equations focus on removing water vapour from the atmosphere inhibiting oxide growth. This project compares the change in oxide layer thickness, composition and structural characteristics, for both the air and NH_4BF_4 atmospheres through the techniques of Rutherford Back Scattering (RBS), X-ray Photoelectron Spectroscopy (XPS), and Auger Electron Spectroscopy (AES). RBS has also been used to determine composition and verify sensitivity factors of XPS and AES.

2. EXPERIMENTAL

Specimens for the experimentation were prepared from hot rolled aluminium sheet of thickness 2.7 mm. Each sample of approximate $11 \times 11 \text{ mm}^2$ dimension was ground to 600 SiC wet paper, to replicate an ingot surface prior to preheating. The samples were ultrasonically cleaned in acetone, and ethanol, and dried with nitrogen. Preheat treatments were conducted in a Tetflow furnace, heating to the maximum temperature over 10 minutes, and then holding constant ($\pm 5^\circ\text{C}$). The experiment investigated preheat treatments at temperatures 480, 500, 520, 540 and 550°C , with samples at each stage being heated for 1, 2, 3, 4, & 5 hours. Ammonium fluoborate was used at a 5 g/m^2 ratio.

RBS was performed using a 2 MeV He^{2+} ion beam at normal incidence to the sample surface and backscattered He particles were collected at an angle of 170° degrees to the incident beam for a total charge accumulation of $100 \mu\text{C}$. The beam spot size was $1.5 \times 1.5 \text{ mm}^2$. RBS spectra were quantified using scattering cross-sections (4) and Rump simulations (5). The oxide thicknesses were determined using simulations in Rump (5). A "mean energy approximation" (4) was used in order to calibrate the depth scale of the oxide coatings on all depth profiles. Scanning AES and XPS were performed on a Fisons Microlab 310F. AES using 10 keV beam energy and XPS using a 300W Mg anode at 60° to the sample surface normal with escaping electrons being collected normal to the sample surface. A 3 keV Ar ion beam at 60° to the surface normal with a current of $100 \mu\text{A}$ per cm^2 was used for ion etching of the samples.

3. RESULTS

RBS has been the major technique used in the analysis of samples, it revealed significant reduction in both the diffusion of magnesium to the surface and the calculated oxide thickness in the presence of NH_4BF_4 . At temperatures above 500°C in air, SEM images revealed depressions and voids due to incipient melting at various stages, around the grain boundaries. Grain boundaries effectively acted as pipes, aiding the diffusion of magnesium to the surface. These results have been verified through compositional analysis with both RBS and AES. Results from NH_4BF_4 atmosphere preheat conditions showed significant improvements.

It was verified experimentally that above 500°C AA5182 alloys undergo incipient melting at the grain boundaries, with magnesium diffusing through to the surface

1. Saied S.O., Sullivan J.L., (1993), *A Study of Thermally Induced Segregation of Magnesium in Aluminium-Magnesium Alloys by means of AES*, J.Phys Condens. Matter, V5 A165-A166
2. *Aluminum, Properties, Physical Metallurgy, and Phase Diagrams*, (1967), American Society of Metals, V1 375
3. Strohmeier B.R., (1989), *Surface Characterization of Aluminum Foil Annealed in the Presence of Ammonium Fluoborate*, Applied Surface Science, V40 249-263
4. Chu W.K., Mayer J.W. and Nicolet M.A., (1978), *Backscattering Spectroscopy*, Academic Press
5. Doolittle L.R., (1986), *Computer Code RUMP*, Nucl. Instr. Meth. B V15 227.