ANALYSIS OF SURFACE COATING ON ALUMINIUM

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INTRODUCTION

The surface treatment of aluminium alloys is essential to the production of durable products. A range of surface modifications are commonly employed: anodising, roller coating and chemical conversion systems in both rinse and no-rinse forms. These surface treatments have been extensively used to provide long term adhesion with lacquers, paints and adhesives. The continued development of these surface treatments has generally been conducted by relating chemical analyses of the surface films to the environmental durability of the coating.

One of the more common forms of conversion coating is based on solutions of chromate, phosphate and fluoride ions. In use, these solutions are known to replace the original air-formed oxide surface by a thicker surface film containing many chemical species. It has been proposed that fluoride ions in solution activate the surface prior to cathodic reduction of Cr$^{6+}$ to Cr$^{3+}$ whilst, at the same time hydrogen evolution occurs. Subsequent precipitation takes place to produce a surface film whose thickness is a balance between dissolution of the outer surface and continued conversion of the substrate metal.

Studies of such surface films have conventionally been conducted using X-ray photoelectron spectroscopy (XPS) analysis in conjunction with ion beam etching to provide through film thickness chemical information. These approaches can, however, suffer from potential confusion as a result of signal averaging over large sampling areas and possible differential chemical and physical degradation of the films due to interactions with the etchant ion beam. Current technology of the physical nature of the film is restricted to that provided by scanning electron microscopy. The approach adapted here involves analysis of the film formed after chemical conversion of aluminium surfaces using XPS and analytical EDX techniques for low atomic number elemental species with limited support from SIMS and LIMA techniques. Thus, an attempt has been made to provide a detailed understanding of the characteristics of these surface films with a view to enhancing environmental stability of coated and bonded products.
MATERIALS AND METHODS

Prior to application of the chromate-phosphate conversion coating the surfaces of a commercial Al-Mg-Si alloy (AA6082) were thoroughly cleaned by vapour degreasing, followed by acid etching. The specimens were subsequently rinsed in deionized water before being immersed in a chromate-phosphate solution at 30°C. Samples were immersed for 10 seconds to provide a nominal film coating weight of 0.2 gm².

XPS analyses of the surface films were conducted in a VG ESCALAB Mark I spectrometer using Al kα X-rays in a vacuum of better than 5 x 10⁻⁷ Pa. Analyses were obtained from a surface area of approximately 16 mm² and from a depth up to 3.0 nm. Low resolution XPS spectra of the surfaces were recorded between binding energies of 0-1000 eV, and high resolution spectra of selected species were recorded over a 25 eV window enabling quantitative surface chemical analysis to be performed.

Analytical transmission electron microscopy of the surface films was conducted on a JEOL 2000 FX operating at 200 KV with a vacuum better than 7 x 10⁻⁵ Pa. TEM specimens were prepared using ultramicrotomy techniques to produce foils of less than 100 nm in thickness. After application of the chemical conversion coating the specimen was encapsulated with an embedding medium. Ultramicrotomed cross-sections were then taken of the aluminium coating-embedding medium to permit examination of the surface chemical conversion coating. High resolution energy dispersive X-ray analysis (EDX) was conducted using condensed electron beam, capable of analysing regions with a surface area of less than 10 nm diameter. The EDX analysis used a windowless detector which enables elements with atomic numbers as low as 7 to be analysed.

SIMS work was carried out at UMIST using a VG SIMS LAB whose features include a VG MIG 100 gallium liquid metal in source and a VG MM 12-12 quadruple mass spectrometer.

The LIMA work was carried out at Cambridge University.

RESULTS/DISCUSSION

Typical low resolution XPS spectra from the surface of the coating is shown in Figure (1).

These spectra identify the main constituents of the outer surface as chromium, phosphorus, carbon and oxygen with low levels of magnesium, aluminium oxide and fluorine also detectable. Depth profiling, using ion beam etching of the conversion coating revealed both the chromium and phosphorus incorporation throughout the film up to the metal-film interface; [Figure 2] but peak in concentration just below the air-film interface.