

Aluminium hydroxide growth on aluminium surfaces exposed to an air/1% NO₂ mixture

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Aluminium samples were exposed to a mixture of 1% NO₂ in air at 100%, 52% and <5% relative humidity. Auger electron spectroscopy depth profiling showed that for the 100% and 52% r.h. environments, the thickness of the surface oxide/hydroxide layer increased linearly with exposure time. X-ray photoelectron spectroscopy was used to study the surface composition as a function of exposure time. The XPS data clearly showed that a transformation from AlOOH to Al(OH)₃ was occurring with time for high humidity exposures. Thick hydroxide layers which formed after prolonged exposure, were also analysed with scanning electron microscopy, thermogravimetric analysis, and X-ray diffraction.

1. Introduction

The low-temperature oxidation of aluminium is known to obey a linear rate law [1] which usually applies during the formation of any porous oxide if the oxidizing gas can diffuse rapidly to the oxide/metal interface [2]. A recent study of the oxidation of aluminium in oxygen showed that oxide films grown at 300 and 640°C do have a fairly high density of defects including cracks and pores [3]. In this study, Auger electron spectroscopy (AES) depth profiling was used to show the interface coarsening that occurred after prolonged oxidation at 640°C. X-ray photoelectron spectroscopy (XPS) analysis showed a difference in the aluminium coordination between low-temperature (amorphous) and high-temperature (crystalline) oxides.

In other recent studies, surface behaviour diagrams were used to present the results of quantitative XPS analysis of the hydration of anodized aluminium surfaces [4, 5]. In a surface behaviour diagram, the composition of a surface is usually represented as the sum of three suitably chosen basis compounds. In one of these studies, the use of a surface behaviour diagram clearly showed that a particular hydration inhibitor displaced water or hydroxyl groups adsorbed on the aluminium oxide surface [5].

In the present study, we report the results of XPS and AES analyses of aluminium surfaces exposed to a mixture of air/1% NO₂ at several different humidity levels. AES depth profiling was used to measure the thickness of the oxide/hydroxide surface layer as a function of exposure time. XPS was used in conjunction with appropriate standards to check the composition of these treated surfaces. A surface behaviour diagram is used to trace the surface composition-exposure time relationship. For surfaces exposed for prolonged periods of time, thermogravimetric analysis (TGA) and X-ray diffraction (XRD) were used to check the composition of the resulting corrosion layer.

2. Experimental methods

Aluminium samples for this study were cut from 4 mil ($\sim 10.16 \times 10^{-5}$ m) thick high-purity foil supplied by A. D. Mackay, Inc. The air/1% NO₂ mixture was supplied by Matheson Gas Products, Inc. The exposures were carried out at room temperature ($23 \pm 2^\circ$ C) in glass chambers capable of being evacuated. The 100% relative humidity (r.h.) environment was created by placing a beaker of distilled water in the chamber. A 52% r.h. environment was created by placing a beaker with a saturated solution of magnesium nitrate in the chamber [6]. Typically, an aluminium sample was placed in the glass chamber, the chamber was evacuated and then the air/1% NO₂ mixture was emitted into the chamber to a pressure of 1 atm.

AES depth profiles were obtained from a Varian scanning Auger spectrometer which has been described elsewhere [7]. An electron beam energy of 5 keV was used to obtain spectra and a 1 keV argon ion beam was used to sputter the samples. The sputter rate for the corrosion coatings which formed was estimated to be 2 nm min^{-1} based on measurements of a thin silicon nitride film on silicon whose thickness had been measured with ellipsometry. XPS spectra were obtained with an extensively modified AEI ES-100 photoelectron spectrometer. Modifications to this instrument have included the addition of a 200 l sec^{-1} turbomolecular pump and a 110 l sec^{-1} ion pump for evacuation of the sample chamber. This instrument is equipped with a magnesium X-ray source.

The TGA data were obtained with a Perkin-Elmer TGS-2. Samples for TGA analysis were heated at $40^\circ \text{ C min}^{-1}$ in a nitrogen atmosphere. X-ray diffraction was performed using a Phillips diffractometer. A boehmite (AlOOH) powder sample (>99.5% pure) supplied by Remet Chemical Corporation was used as a standard for the XRD and XPS studies. XRD analy-

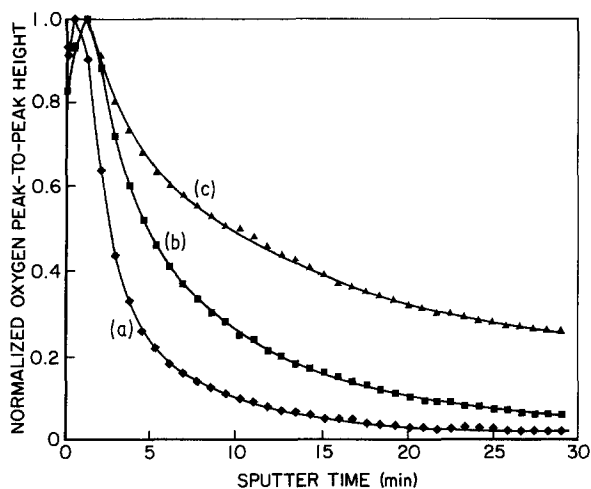


Figure 1 Normalized oxygen AES peak-to-peak heights for aluminium samples aged in air/1% NO₂ at 100% r.h. for (a) 0 min, (b) 40 min, and (c) 80 min.

sis of this sample showed excellent agreement with reported data [8] and established that no other phases were present. An 0.3 μm alumina (Al₂O₃) powder from Buehler Ltd was also used as a standard for XPS.

3. Results and discussion

3.1. AES studies of oxide/hydroxide thickness

Fig. 1 shows AES depth profiles of oxygen levels on aluminium samples exposed to air/1% NO₂ at 100% r.h. for 0, 40 and 80 min. For the purposes of this study, we have defined the oxide/hydroxide thickness by the point in the profile at which the oxygen signal falls to 37% (1/e) of its maximum value. Fig. 2 gives these oxide/hydroxide thicknesses as a function of exposure time for aluminium samples aged in air/1% NO₂ at 100%, 52%, and < 5% r.h. The least-squares linear fits to the 52% and 100% r.h. data (for exposure times greater than 20 min) shown in Fig. 2 have correlation coefficients of 0.89 and 0.98, respectively. Note that no growth of the oxide/hydroxide layer was observed for ageing times up to 52 h at < 5% r.h.

3.2. XPS studies of film composition

Using relative sensitivity factors of 0.60 and 0.18 for

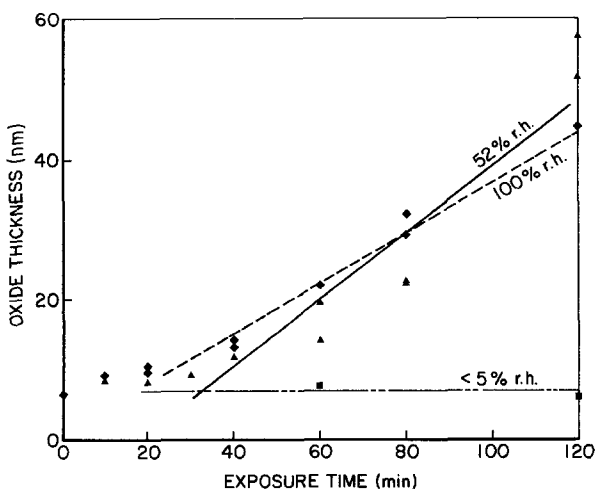


Figure 2 Oxide/hydroxide thicknesses on aluminium samples aged in air/1% NO₂ at (◆) 100% r.h., (▲) 52% r.h. and (■) < 5% r.h.

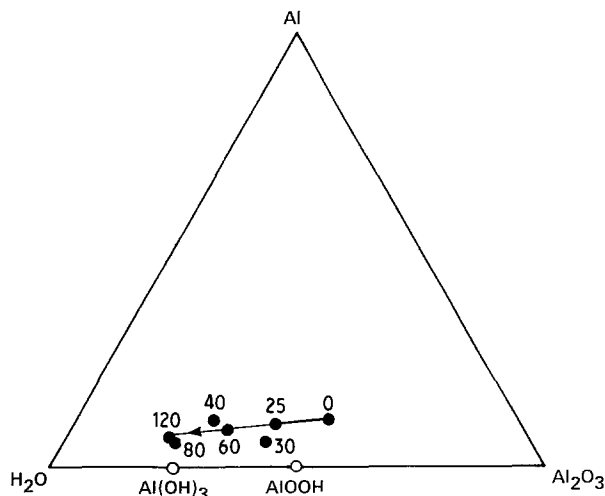


Figure 3 Surface behaviour diagram for aluminium exposed to air/1% NO₂ at 100% r.h. (Numbers shown next to points are ageing times in minutes.)

the O 1s and Al 2p peaks, respectively, the oxygen-to-aluminium ratios were calculated to be 1.48 for the alumina and 1.97 for the boehmite. These are quite close to the expected values of 1.5 and 2.0.

Fig. 3 shows an Al₂O₃-Al-H₂O surface behaviour diagram for the exposure of aluminium to air/1% NO₂ at 100% r.h. Note that the surface composition is close to AlO(OH) for ageing times less than 30 min. For ageing times greater than 30 min, the composition gradually changes to Al(OH)₃. For an ageing time of 120 min, some aluminium metal is still detected with XPS, even though the AES profiling data showed the average oxide/hydroxide thickness to be greater than 40 nm. Apparently, this oxide/hydroxide layer is not uniform and contains cracks. These cracks are probably the result of shrinkage of the hydroxide layer caused by dehydration within the XPS vacuum system.

3.3. Studies of thick oxide/hydroxide films

Fig. 4 shows a scanning electron micrograph of the surface of an aluminium foil sample which had been exposed to air/1% NO₂ at 100% r.h. for 7 days. Note that the hydroxide layer loosely adheres to the substrate and, in fact, has delaminated completely in many

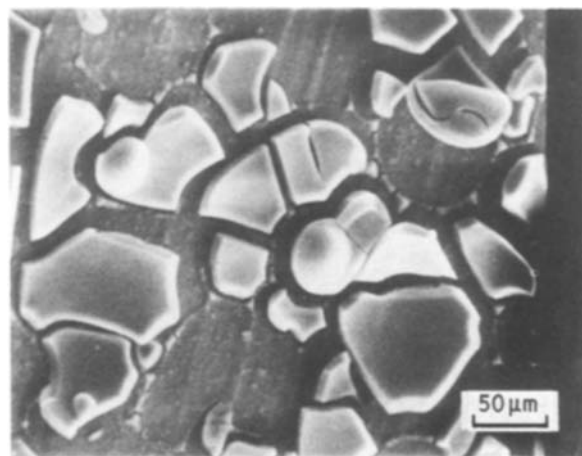


Figure 4 Scanning electron micrograph of aluminium foil sample exposed to air/1% NO₂ at 100% r.h. for 7 days.

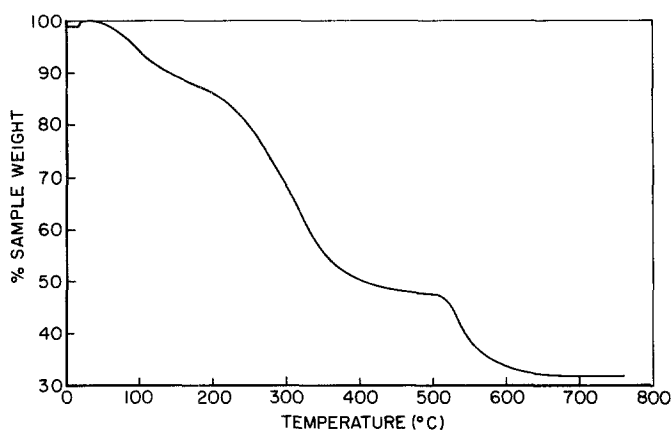
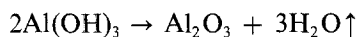
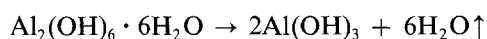
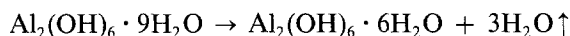


Figure 5 Weight loss curve for corrosion product collected from surface of aluminium foil aged in air/1% NO₂ at 100% r.h. for 7 days.

areas. The poor adhesion between an AlOOH layer and an aluminium substrate has been observed in a previous study [4].

A TGA analysis was performed on the corrosion product collected from the surface of a sample aged in air/1% NO₂ for 7 days. Fig. 5 shows sample weight as a function of temperature for this corrosion product. Three steps in its decomposition are clearly evident. A possible decomposition mechanism which would be consistent with the TGA data is:



This decomposition mechanism would give steps at 84%, 49% and 32% of the original sample weight. This is in good agreement with the TGA data.

XRD analysis of the corrosion product previously analysed by TGA showed fair agreement with a reported pattern for Al₂(OH)₆ · H₂O. No reported pattern for Al₂(OH)₆ · 9H₂O was available for comparison. From the XPS results presented in the previous section, it was concluded that a surface composition of Al(OH)₃ resulted for samples aged longer than 80 min in air/1% NO₂ at 100% r.h. To reconcile the XPS results with the TGA results it must be concluded that the water of hydration is apparently removed by the XPS vacuum system before the analysis even begins.

Another recent study has shown that during ultrahigh vacuum ageing there are changes in the composition of aluminium surfaces which had been polarized in Na₂SO₄ solutions [9]. Specifically, a gradual transformation from Al(OH)₃ to AlOOH was observed during 7 days of ageing. However, neither this study [9] nor previous studies [4, 5] have mentioned that there may be some additional water of hydration on Al(OH)₃ surfaces which will be rapidly removed in ultrahigh vacuum.

4. Conclusions

The XPS and TGA results, when combined, show that a layer of hydrated Al(OH)₃ is formed on aluminium samples aged in a humid atmosphere of air/1% NO₂.

When the XPS data are plotted on a surface behaviour diagram, it can be seen that the surface changes from an initial composition of AlOOH to one of Al(OH)₃ after ageing for 80 min or more at 100% r.h. The AES results show that the growth of the hydroxide layer is in good agreement with a linear rate law for ageing times greater than 20 min in both 52% and 100% r.h. environments. There was no oxide/hydroxide layer growth for samples aged in air/1% NO₂ at < 5% r.h.

Neither XPS nor AES showed the presence of significant amounts of nitrogen on any of the aluminium surfaces exposed to air/1% NO₂. This may be somewhat unexpected, because a recent study of aluminium corrosion in nitric acid has suggested that hydrated aluminium nitrate is a likely reaction product [10].

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