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The Etching of Aluminium Alloy 2024-T3 in a Non-chromate Fe(III)-HF-HNO_3 Deoxidiser: an Atomic Force and Scanning Kelvin Microscopy Study.

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Abstract

Following the treatment with a commercial non-chromate deoxidizer, the surface of aluminium alloy 2024-T3 has been characterized using a series of techniques (atomic force microscopy, scanning Kelvin probe force microscopy, scanning electron microscopy and X-ray photoelectron spectroscopy). The Fe(III)-HF-HNO_3 deoxidizer was shown to remove a significant proportion of intermetallic particles from the surface for immersion times longer than 5 minutes. Scanning Kelvin probe force microscopy confirmed the relative absence of metallic copper on the surface of polished 2024-T3 after 10 minutes deoxidation. High values of contact potential associated with pits and trenches on deoxidized surfaces were found to be artifacts generated as a result of the inability of the AFM tip to accurately map the surface topography

1. Introduction

The need to establish less toxic alternatives to chromate conversion coatings has driven a large number of investigations into conversion coating deposition and protective mechanisms. In addition, recent advances in scanning probe microscopy techniques have allowed more detailed research regarding the influence of surface microstructure on coating formation and their resultant properties. The modification of atomic force microscopy (AFM) to provide simultaneous scanning Kelvin probe (SKPFM) measurements has made it possible to resolve surface potential differences on alloy surfaces with a lateral resolution of less than 50 nm. Several studies have investigated the application of SKPFM to characterise the intermetallic species on 2024, revealing that localized potential differences of up to 400 mV exist between copper-containing intermetallic phases and the aluminium matrix [1-6]. Whilst the contact potential difference (CPD) measured in air with SKPFM does not provide a quantitative evaluation of the solution-based open-circuit potential [7], it does provide an indication of the extremes of local potential differences [1-2]. Importantly, SKPFM has the ability to evaluate the relative potentials of different metallic phases on an individual sample. Therefore, SKPFM provides a means to ‘fast-track’ the characterization of alloy microstructures in terms of their propensity for localized corrosion, and is envisaged as a key support tool for future alloy development and joining technology research.

In this study we utilize SKPFM to characterize the surface of 2024-T3 during non-chromate deoxidation. As it happens there are many reports on the deposition of non-chromate coatings yet limited published information is available regarding non-chromate deoxidation processes [8]. Here, the surface characteristics of 2024-T3 are detailed after immersion in a non-chromate Fe(III)-HF-HNO_3-based deoxidizer for times ranging from 1 to 10 minutes at ambient temperature. The ability of the deoxidizer to remove alloying metals, particularly Cu, from the surface is discussed. Also, particular emphasis is placed on analyzing the information obtained using SKPFM, whilst scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) were utilized to provide further detail of the surface state.

2. Experimental

Sheets of 2024-T3 (Kaiser Aluminum) were cut into 50 x 10 x 1.6 mm samples (compositional details are given in Table 1). Polished samples were achieved using a sequence of diamond pastes (15 μm, 3 μm and 1 μm) and OP-S (Struers) oxide polish. The Fe(III)-HF-HNO_3 deoxidising formulation (Turco SmutGo NC-B) was supplied as a dark brown concentrate by Elf-Atochem (Australia), and was diluted to 28 %v/v and used at ambient temperature (ca 21°C). The manufacturers specifications indicate that satisfactory deoxidation can be obtained over a concentration range of 10-28 %v/v, thus a heavy etch-rate deoxidation regime was chosen to emulate etch-rates for common chromate containing deoxidisers [9].

AFM-SKPFM was performed on a Digital Instruments Nanoscope III Multimode instrument with an Extender™ electronics module. Contact potential differences captured using a Lift-Mode™ height of 100 nm, and scaled relative to the Pt-coated silicon cantilever tip (NT-MDT). SKPFM image processing was aided by WSxM© analysis software (Nanotec Electronica, http://www.nanotec.es). Details of SEM and XPS procedures can be found elsewhere [9].

3. Results and Discussion

3.1 The Non-Chromate Deoxidation of 2024-T3

Figure1 demonstrates the typical features that exist on the untreated surface of 2024. Features include two main constituent phases (Al_2MgCu and a mixture of Al-Cu-Fe-Mn phases) with sizes in the range of 2 – 30 μm. Also, smaller dispersoid phases ($Al_{20}Cu_3Mn_2$) with sizes in the range of 100 – 500 nm. The electrochemical potential of Al_2MgCu (S-phase) has been reported to be more anodic than the matrix [12], thus making these particles preferential sites for localized attack. In contrast, Al-Cu-Fe-Mn intermetallics have an electrochemical potential cathodic to the aluminium matrix [6]. Figure1b shows both S-phase and Al-Cu-Fe-Mn intermetallics to have a lower CPD (200-300 mV) than the surrounding aluminium matrix after polishing, a result that is consistent with other studies [4-6]. The CPD over dispersoid particles was found to be approximately 50-70 mV lower than the matrix. The low CPD's for constituent and dispersoid particles is thought to be a reflection of the significant Cu concentrations in these phases.

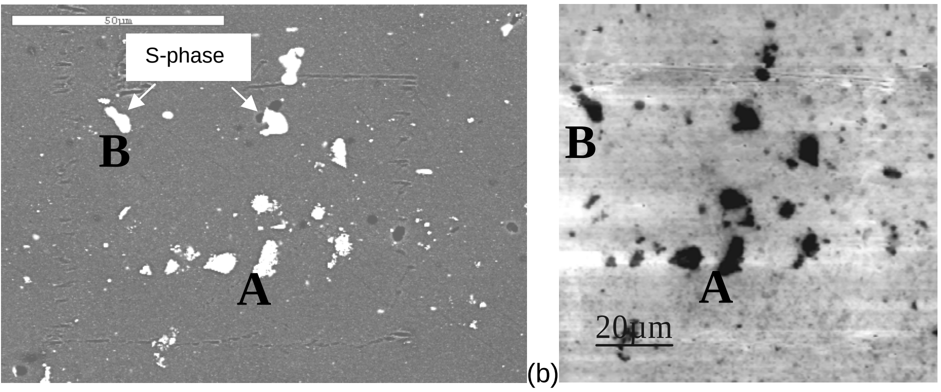
(a) (b)

Figure 1: Characterisations of polished 2024 with (a) Backscattered SEM and (b) SKPFM potential image.

Figure 2 summarises the state of the 2024 surface after Fe(III)-HF-HNO_3 deoxidation for 1 min, 5 min and 10 min. After 1 minute deoxidation, there was evidence of shallow pits in the surface (< 600 nm). Backscatter and secondary electron images revealed incomplete etch-out and occluded etch pits, and indicated that many intermetallics remained on the surface, including constituent particles and inclusions (typically 10-30 µm) as well as dispersoid particles (typically 100-500 nm). Potential maps confirmed the presence of intermetallics and revealed that the majority of intermetallics retained a CPD approximately 250 mV lower than the matrix. Some shallow pits (100 - 200 nm depth) had decreased CPD in comparison with the surrounding matrix (A) whilst others demonstrated increased potential differences (B). XPS analysis on rolled 2024-T3 sheet (alkaline cleaned and exposed to identical deoxidation treatments) revealed that a 1 min immersion led to an increase in Cu and Mn on the surface and a removal of silicates remaining from alkaline cleaning (Table 1). The article by Hughes et al. [9] contains further detail on the XPS analysis of rolled 2024-T3. The Cu 2p3/2 spectrum suggested a mixture of oxidation states, with at least Cu^{I} and Cu^{II} present on the surface. Fe is likely to be present as Fe^{2+}, resulting from the precipitation of hydrated iron oxides due to pH increases during rinsing. Mg was not greatly affected by the deoxidizer after 1 minute of deoxidation, suggesting a protective overlying layer of either hydroxide or magnesium fluoride.

AFM images of the surface after 5 minutes deoxidation at room temperature showed levelling of the nodular oxide deposits observed after 1 minute deoxidation (Fig 2). The etching of the constituent particles was more extensive and the etch pits or trenches around these particles are broader and more open than after 1 minute's deoxidation. Average trench depths were found to be approximately 200 nm deep. Some etch pits with depths greater than 2 µm were of a similar size and shape to $CuMgAl_2$ particles (C) and may indicate that these particles were preferentially removed. Potential maps showed Al-Cu-Fe-Mn intermetallics to maintain lower CPD's (-145 mV) than the matrix, whilst etch pits thought to be associated with S-phase particles showed apparent CPD's 100 - 150 mV greater than the matrix. Cu levels on rolled 2024 were observed to increase compared to 1 minute immersion, which may arise from the redeposition onto the matrix, or the dissolution of surface oxides revealing sub-surface Cu containing intermetallics [6]. XPS indicated that Cu existed as a mixture of Cu^{I} and Cu^{0} species after 5 minutes deoxidation. Mg levels were substantially reduced after 5 minutes of deoxidation and there was evidence of further Fe build-up in the form of $Fe^{2+/3+}$ on the surface with the levels increasing with longer deoxidation.

Table 1: XPS analysis of rolled 2024-T3 surface after alkaline clean and deoxidation.

	Alloy Component (at.%)						
	Al	O	Cu	Mg	Mn	Si	Fe
None (Bulk)	93.0	-	5.3	1.6	0.6	0.06	0.2
Alkaline Clean	18.8	65.4	0.1	2.8	0.6	12.0	-
1 min	23.7	68.1	1.2	2.2	1.1	0.9	0.4
5 min	36.0	55.4	3.5	0.3	0.8	-	0.7
10 min	27.2	60.8	0.3	-	1.1	0.6	0.6

After 10 minutes deoxidation the surface exhibited a large number of etch pits (e.g. E) with depths exceeding 2.5 μm (Figure2). As observed after 5 minutes deoxidation, potential maps showed increased CPD's at etch pit sites, an occurrence that is discussed below. Backscatter images of the alloy surface after 10 minutes of deoxidation showed that only a few constituent particles remained on the surface. Al-Cu-Fe-Mn phases (e.g. D) lay a shallow depth (approximately 200 nm) below the level of the matrix, and possess a CPD within 100 mV of the matrix. XPS analysis of rolled 2024-T3 after 10 min deoxidation suggested that only O and Al are detected in significant amounts. Whilst the predominant form of copper was demonstrated to be metallic, its levels on the surface are decreased significantly. Iron was also shown to exist in metallic form. SKPFM images on polished 2024-T3 was not able to confirm the presence of metallic Cu, which has been observed on rolled 2024-T3 exposed to identical deoxidising conditions [9] and other solution environments [4].

3.2 Contact Potential Measurements Over Etch Pits

Analysis of Figure 2 reveals that the CPD associated with etch pits varied as a function of deoxidation time. After 1 min, shallow pits displayed both high and low CPD's compare to the aluminium matrix. However, after 5-10 min deoxidation the CPD over etch pits was significantly greater than that of the matrix, suggesting that these regions are less noble in their electrochemical potential. Our investigations have shown that some high CPD's near pits may be associated with artifacts resulting from poor height imaging. Figure3a and 3b show the simultaneously collected height and potential information collected over a pit at scan angles of 0 and 90º. The data collected in both scan directions shows that where the cantilever tip fails to trace the pit geometry in the height image, a high CPD is displayed in the potential image. The artificially increased CPD is likely to be the result of an increased sample-tip separation compared to the set 'lift' height of 100 nm. Errors caused by the failure to accurately trace the topography are likely to be enhanced for increased scan rates and areas. To date most SKPFM studies investigating 2024 have been carried out using large scan sizes greater than 50 µm. However, future studies involving CPD measurements may benefit by inspecting pits at higher magnifications to ensure accurate data. Our studies showed that transformation of the height image to a derivative image provided a good indication of whether the topography of the pit was realized.

That is, flat areas in the derivative image indicate a poorly detailed height image. Figure3c demonstrates that not all high CPD's near etch pits are associated with artifacts. For this particular example the high CPD (+200 mV to the matrix) near A is thought to be a result of either the deposition of a thin film of Mg/MgF_2 or Fe metal, or due to localized oxide thinning (oxide thickening decreases CPD [2]).

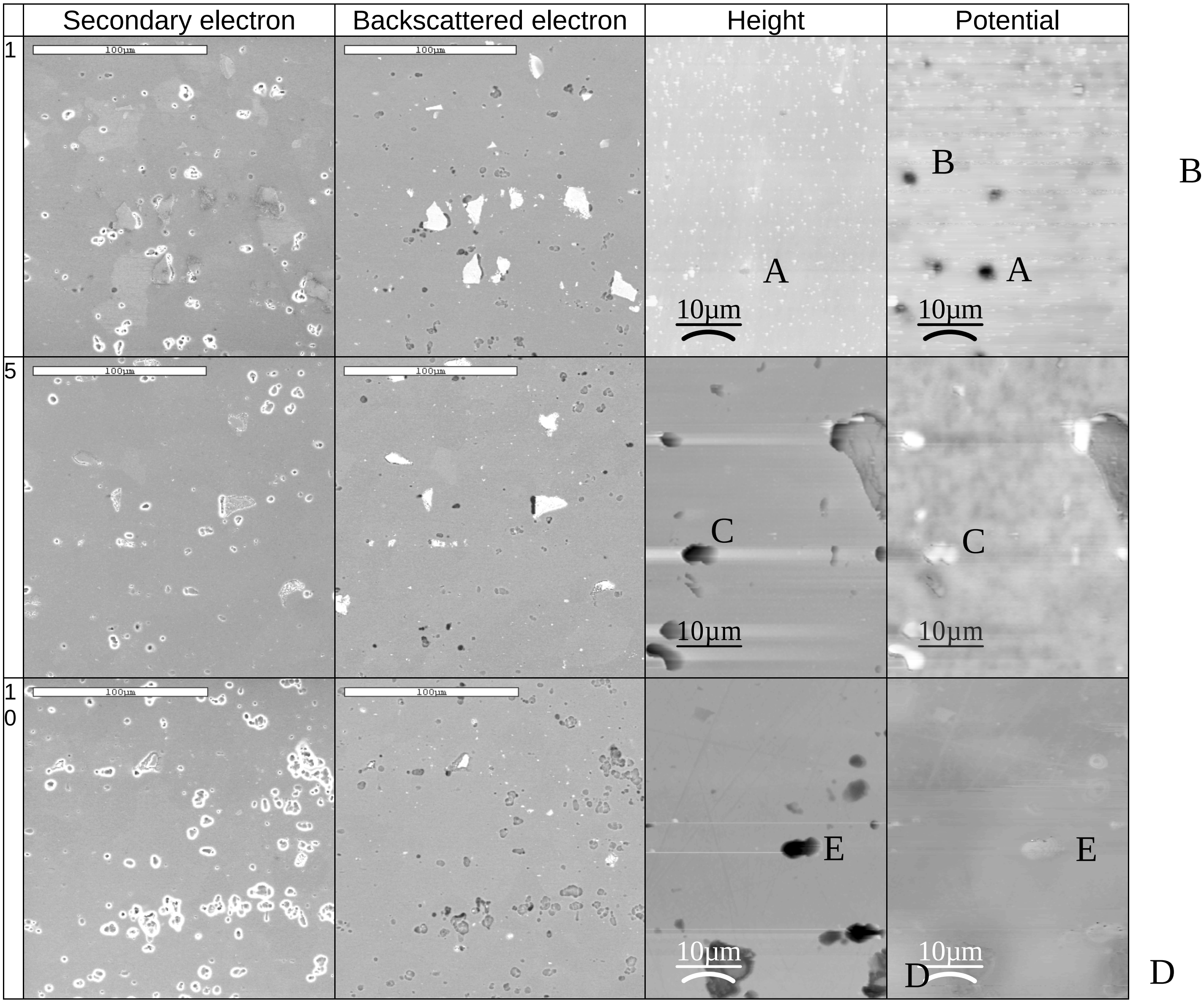

Figure 2: SEM and AFM-SKPFM characterizations of polished 2024 after 1, 5 and 10 minutes deoxidation.

4. Summary

SEM and SKPFM data have shown that after a 1 minute immersion in the Fe(III)-HF-HNO_3 deoxidizer at room temperature, there is attack of the oxide covering the matrix but only limited attack on intermetallics. After 5 minutes immersion there was greater attack of the matrix oxide and indirect evidence for removal of $CuMgAl_2$. After 10 minutes deoxidation, there was a similar extent of reaction on the matrix as for 5 minutes but this was accompanied by nearly complete removal all types of intermetallics. Potential images collected using SKPFM were found to show increased contrast for the presence of copper-containing intermetallics. In addition, artificially high CPD's were found to exist over deep pits.

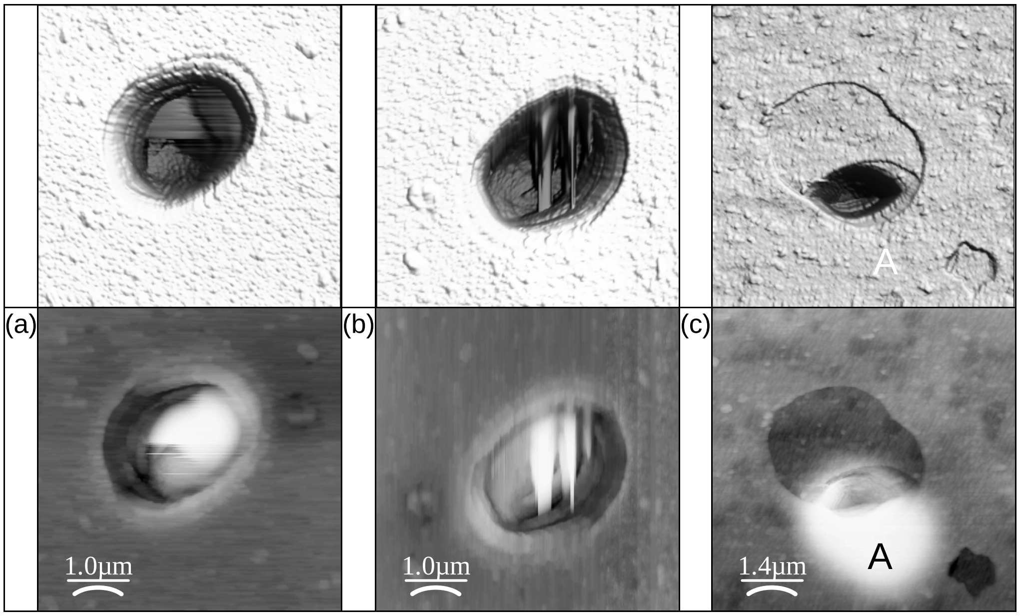

Figure 3: SKPFM height (top) and potential (bottom) images: (a) Pit after 5 min immersion, 0º scan angle, (b) Pit after 5 min immersion, 90º scan angle, (c) Pit after 10 min immersion.

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