

Influence of nitric acid pre-treatment on Al–Cu alloys

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Abstract

The enrichment of copper alloying additions near the surface of sputtering-deposited Al–1.3 at.%Cu, Al–2.7 at.%Cu and Al–30 at.%Cu alloys is investigated following immersion in nitric acid, which is used commercially as a de-smutting pre-treatment. Corrosion of the alloys is revealed at rates in the range 4–13 nm min⁻¹, leading to enrichment of copper in the alloy surface regions. Enrichments are also generated by nitric acid treatment of AA2024-T3 and AA7075-T6 alloys, with levels similar to those achieved by etching in sodium hydroxide solution. Conventional durations of de-smutting treatments in nitric acid have minor influences on the magnitude of enrichment.

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1. Introduction

The pre-treatment of aerospace aluminium alloys prior to application of conversion coatings commonly involves etching in sodium hydroxide followed by de-smutting in nitric acid [1,2]. The pre-treatment can affect the composition of the alloy surface and hence, the development of the conversion coatings [3,4]. Etching usually removes several microns from the alloy surface, leaving exposed regions of residual second phase and alloy matrix, the latter with a scalloped texture [5]. A layer of hydrated alumina is left on the alloy, which is dissolved by de-smutting. Etching and conversion treatments can also enrich alloying elements that are noble with respect to aluminium, such as copper in AA2000 and AA7000 series [6]. The enrichment, located in a ~2 nm-thick alloy layer just beneath the surface oxide film, arises from preferential oxidation of the aluminium [7,8]. At a critical enrichment, dependent upon the concentration of the particular alloying element, the alloying element can be incorporated into the film either as oxidized species [9] or as metallic nanoparticles [10]. The critical enrichment possibly differs slightly depending upon whether or not the alloying ele-

ment is oxidized. An enrichment of ~40 at.% Cu is generated for a solid-solution Al–1 at.%Cu alloy [8]. However, for copper-rich second phase, critical levels are achieved at levels relatively close to the composition of the bulk phase [11]. In ternary and higher alloys, interactions between co-enriching alloying elements may modify the critical enrichments of the individual alloying elements. Once the critical enrichment is achieved, the average concentration of the alloying element in the enriched layer remains approximately constant during continued oxidation of the alloy [7]. Generally de-smutting is used to remove residues of prior etching. However, the time of de-smutting may affect the subsequent protection of the alloy by conversion coatings [12]. Concerning de-smutting, no studies have been carried out of its influence of nitric acid on enriching of alloying elements. The present work examines its effect in AA2024-T3 and AA7075-T6 commercial alloys and sputtering-deposited Al–Cu alloys with compositions approximately representative of matrix regions and Al₂Cu phase of commercial alloys.

2. Experimental

Binary Al–Cu alloys, containing 1.3, 2.7 and 30 at.%Cu, were deposited on to 99.99% aluminium substrates, of dimensions 2.5 cm × 1 cm, using an Atom Tech magnetron sputtering

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Table 1
Chemical composition of the AA 7075 and AA2024 alloys (wt.%)

	Al	Zn	Cu	Mg	Mn
AA2024-T3	bal	0.25	3.8–4.9	1.2–1.8	0.30–0.9
AA7075-T6	bal	5.1–6.1	1.2–2.0	2.1–2.9	0.30

facility. The system was first evacuated to 3×10^{-7} mbar, with deposition subsequently carried out in 99.999% argon at 5×10^{-3} mbar. The aluminium substrates were electropolished in ethanol/perchloric acid solution to a mirror finish. The thicknesses of the deposited alloy layers were in the range 340–580 nm. Following masking, the deposited alloys were immersed for 30 or 900 s in 300 ml/l of 70% nitric acid at ambient temperature. A piece of each substrate with deposited alloy was retained without immersion to determine the initial thickness of the alloy. Commercial AA7075-T6 and AA2024-T3 alloys, of 2 mm thickness and of nominal compositions shown in Table 1, were polished to a 1 μ m diamond finish, degreased in ethanol and immersed in nitric acid, using the same conditions as employed for the binary alloys. In some cases the alloys were etched for 180 s in 20 g/l sodium hydroxide solution at 43 °C after mechanical polishing and then de-smutted in nitric acid. Open-circuit potentials of the various specimens were measured with respect to a saturated calomel electrode during immersion in nitric acid.

The binary alloys, prior to and following immersion in nitric acid, were sectioned by ultramicrotomy and examined by transmission electron microscopy (TEM), using a JEOL FX 2000 II instrument. The specimens of commercial alloy were examined by field emission gun scanning electron microscopy (FEG-SEM) using a JEOL 6500F instrument equipped with facilities for energy dispersive X-ray (EDX) analysis. Medium energy ion scattering (MEIS) measurements were made using 100 keV He⁺ ions from the facility of Daresbury Laboratory. The ion beam was of dimensions 1 mm \times 0.5 mm. The data were interpreted using SIMNRA software. The enrichments determined by MEIS have an accuracy of \sim 10%.

3. Results

3.1. Enrichment of copper during immersion of binary Al–Cu alloys in nitric acid

Copper enrichment due to immersion in nitric acid was investigated using Al–1.3 at.%Cu and Al–2.7 at.%Cu alloys. Prior to immersion, MEIS disclosed enrichments of 1.9×10^{14} and 3.7×10^{14} Cu atoms cm⁻² respectively, located beneath oxide films of thickness \sim 4 nm (Fig. 1(a,b)). These enrichments can be accumulated by oxidation of \sim 2.4 and 2.3 nm of the alloys respectively, consistent with formation of air-formed oxides of a few nanometres thickness. Following immersion in nitric acid for 30 s, respective enrichments of 1.7×10^{14} and 9.3×10^{14} Cu atoms cm⁻² indicated negligible change for the Al–1.3 at.%Cu alloy and a small increase for the Al–2.7 at.%Cu alloy (Fig. 1(a,b)). The increased enrichment of the Al–2.7 at.%Cu alloy arises from further oxidation

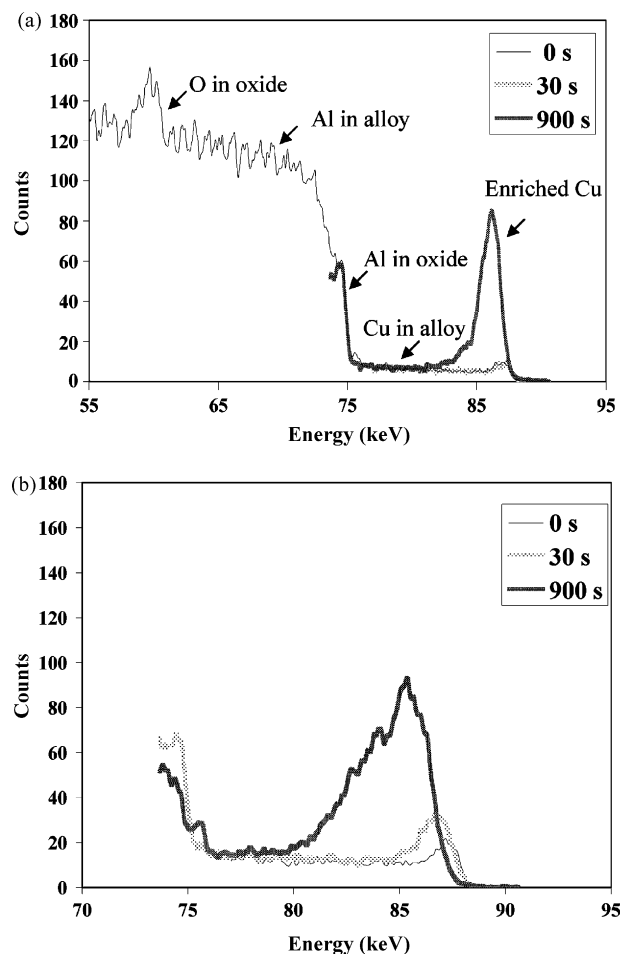


Fig. 1. MEIS spectra for (a) Al–1.3 at.%Cu and (b) Al–2.7 at.%Cu alloys prior to and following immersion for 30 and 900 s in 30 ml/l 70% nitric acid at ambient temperature. The spectrum of (a) includes scattering from the aluminium and oxygen, while that of (b) is confined to the scattering from copper in the alloy and the enriched alloy layer.

of \sim 3 nm of the alloy. The enrichments rose to 3.1×10^{15} and 5.0×10^{15} Cu atoms cm⁻² respectively after immersion in nitric acid for 900 s (Fig. 1(a,b)). These amounts of copper are contained in \sim 40 and 31 nm of the alloy respectively.

Examination of the Al–1.3 at.%Cu and Al–2.7 at.%Cu alloy surfaces by SEM disclosed the faceted, nanocrystalline grains of the sputtering-deposited layer following immersion for 30 s in nitric acid (Fig. 2(a,b)). The dimensions of the grains, which are shown in later TEM to be columnar, were typically in the range 40–130 nm. The presence of the faceted grains is consistent with the limited corrosion indicated by MEIS. The grains were more distinct for the Al–1.3 at.%Cu alloy than for the Al–2.7 at.%Cu alloy, possibly due to a slightly increased corrosion of the latter alloy. With treatment in nitric acid for 900 s, relatively numerous shallow cavities, which were approximately circular and of diameter up to \sim 100 nm, were present on the surface of the Al–1.3 at.%Cu alloy (Fig. 3(a)). Regions between cavities revealed discontinuous linear features, appearing light in the micrographs. For the Al–2.7 at.%Cu alloy, the linear features formed an extensive network with dimensions possibly related to the grain size (Fig. 3(b)). At reduced magnification, occa-

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