Effect of surface preparation treatments on copper enrichment on 2024 aluminium alloy surface

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Abstract

X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) were used to analyse the surface modifications of AA-2024-T3 induced by model pre-treatment baths such as H₂SO₄, HNO₃, and in a mixture of both acids. These acids are commonly used for pickling treatment, applied before conversion coating deposition.

ToF-SIMS and XPS measurements showed a significant copper enrichment in metallic and oxidised states, localised at the oxide/metal interface. The sulphuric acid treatment led to the highest Cu enrichment. A lower dissolution rate of AA-2024 was observed by inductively coupled plasma optical emission spectroscopy (ICP-OES). It was concluded that the surface enrichment in Cu is mainly associated with dealloying of intermetallic particles by selective dissolution of the less noble elements.

Keywords: aluminium alloy 2024-T3; surface pre-treatment; copper enrichment; XPS; ToF-SIMS

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1 Introduction

High strength aluminium alloys are widespread in aircraft industry for their low weight and good mechanical performance due to the addition of alloying elements in the aluminium matrix such as Cu, Fe and Mg. The AA-2024-T3 is one of the most commonly used alloys for the fuselage [1]. The intermetallic particles formed by precipitation of alloying element provide active sites for the localised corrosion due to their either cathodic (θ - Al_2Cu) or anodic ($\text{S-Al}_2\text{CuMg}$) nature relative to the surrounding matrix [2]. Thus, a coating is needed for good corrosion protection of these alloys.

For the last few decades, corrosion protection has been provided by chromate conversion coating or anodising. Hexavalent chromate conversion coatings (CCC) were the most applied anticorrosive treatments for aluminium alloys [3]. Due to the toxicity of chromium (VI), alternative corrosion inhibitors have been developed such as trivalent chromium, rare-earth, permanganate, molybdate or vanadate -based conversion coatings [3–11]. The conditions to obtain an optimal conversion coating are not clearly understood due to lack of knowledge on coating formation mechanisms. The conversion coating formation is strongly influenced by the alloy surface preparation, which appears as a key step for the conversion process [4,7,12,13].

Surface preparation is known to influence the properties of the coatings [4,12–17]. The pre-treatment should allow to remove lubricant to clean the surface, standardize and control the chemical composition of the alloy surface to improve conversion coating performances. Prior to the conversion, two types of pre-treatments by immersion are usually used. First, a degreasing allows to clean the surface by removing some greases and fabrication oils.

Second, pickling/deoxidizing/desmutting, which denote the same process, allow to remove the oxide layer and the intermetallic particles and to form a new, fresh oxide.

An acid deoxidizer often contains nitric acid to dissolve the oxide film. However nitric acid is not sufficient to remove all intermetallic particles, and it is often used with other acids such as sulphuric acid, phosphoric acid, hydrofluoric acid or bromic acid. During deoxidizing, the attack can lead also to the nanotexturing of the matrix, generally denoted as a scalloped surface [18]. The cathodic particles undergo trenching of the surrounding matrix and the anodic intermetallic particles are subject to the dealloying mechanism. Due to the dealloying the intermetallic particle more cathodic potential can be observed and trenching occurs in the matrix [2,19]. Many authors provided evidence of a copper enrichment at the surface during acid deoxidizing [4,12,20–23]. Moffit *et al.* [21] studied the evolution of alloying element content during various surface preparations and showed that the highest quantity of Cu enrichment occurs in the case of HNO₃-HF deoxidizing process without degreasing. Viroulaud *et al.* [4] observed a Cu enrichment beneath the oxide after degreasing and deoxidizing attributed to a selective dissolution of Al and Mg occurring principally in IMPs, with possible release of copper. Liu *et al.* [23] found a copper enrichment increased by a factor of 15 between 30 s and 300 s immersion of 2024-T3 in nitric acid. The formation of around 1 nm-thick copper layer at the oxide/Al-Cu metal interface after 300 s of immersion in nitric acid was also evidenced.

The surface preparation and the conversion treatment should perfectly match to grow a resistant coating. In fact, all deoxidizers are not adapted to all conversion processes [12]. Authors have shown alteration of the coating's homogeneity, which can be explained by aggressive conditions of deoxidizers and too long immersion time [4,13]. There are only few

studies on the influence of copper enrichment on the coating deposition and the corrosion properties. Verdalet-Guardiola *et al.* [15] demonstrated that the copper enrichment led to a less protective coating whereas Viroulaud *et al.* [4] showed that a strong Cu enrichment on AA-2024 alloy was not detrimental for coating quality.

The aim of this work is to determine the role of nitric and sulphuric acids, which are mainly present in deoxidizing baths and particularly in the sulfo-nitro-ferric baths, on the chemical composition of the surface of a 2024-T3 aluminium alloy. The surface morphology, chemistry and the constituent dissolution of a 2024-T3 alloy after deoxidizing were investigated in details. Three deoxidizer baths were tested: nitric and sulphuric acids alone and the mixture of both acids.

2 Experimental

2.1 Materials

High strength aluminium alloy AA-2024-T3 was chosen to investigate acid bath pre-treatments. The specification of 2024 alloy is: Cu (3.8–4.9 wt%), Mg (1.2–1.8 wt%), Mn (0.3–0.9 wt%), Fe (0.5 wt%), Si (0.5 wt%), Zn (0.25 wt%), Ti (0.15 wt%), Cr (0.1 wt%), and Al (balance). The T3 thermal treatment is a solution treatment (at 495 ± 5 °C) followed by a cold strain-hardening and finished by aging at ambient temperature for minimum 4 days. 1 mm-thick rolled sheet panels obtained from the IRT-M2P (France) were used as substrates. Substrates were cut in 1×1 cm² samples.

A pure aluminium 99.9999% purchased from Goodfellow was used to perform comparative studies with results obtained on 2024-T3. A 3 mm thick panel was used. Samples were cut in 1×1 cm² square sheets.

Substrates were grinded with SiC grinding paper from 1200 to 2400 grades. Then, they were polished with alumina paste ranging from 2-3 μm to 0.5 μm . This mirror-finish surface before and after pre-treatments was necessary for XPS, ToF-SIMS and SEM analyses. The other side of the sample was grinded with SiC paper 1200 to have similar surface finishing and reactivity in the pre-treatment baths used for analysis by ICP-OES. Solvent cleaning in ultrasonic bath was done during 2 min in propan-2-ol and then 2 min in ethanol.

Three pre-treatment baths were used: 100 g/L HNO_3 , 150 g/L H_2SO_4 and a mixture of both acids in same concentration ranges. These concentrations have been chosen to be comparable with the Socosurf bath, which is a HNO_3 - H_2SO_4 -Fe(III) commercial bath. The baths were diluted with ultra-pure Millipore® water (resistivity of 18.1 $\text{M}\Omega\cdot\text{cm}$). Samples were immersed in 75 mL baths during 10 min at 50 °C and rinsed during 2 min in ultra-pure water. Then, they were dried under filtered compressed air. They were quickly transferred to the analysis (in less than 1 hour).

2.2 XPS, ToF-SIMS, SEM and ICP-OES characterizations

Surface chemical analyses were performed with an XPS Thermo Electron Escalab 250 spectrometer. The vacuum was below 2×10^{-9} mbar during analysis. A disk of around 500 μm of diameter is analysed with a take-off angle of 90°. X-Rays were provided from a monochromatic Al $\text{K}\alpha$ source ($h\nu = 1486.6$ eV). Acquisitions of survey spectra with a pass energy of 100 eV and high-resolution core level spectra (Al 2p, Al 2s, Cu 2p, Mg 1s) and Auger spectra (Cu LMN) with a pass energy of 20 eV were performed. Calibration of the spectrometer was carried out with Au 4f_{7/2} at 84.1 eV. The Advantage™ software (Thermo ElectronCorp.) was used to fit the spectra with a Shirley type background and

Lorentzian/Gaussian 30/70 peak shape for oxides. The CasaXPS processing software was also used for the fitting of Cu LMN spectra.

A ToF-SIMS V spectrometer (Ion ToF GmbH) operating at 10^{-9} mbar vacuum was used to perform in-depth profile analysis. The depth profiles were obtained using a dual beam mode: a pulsed 25 keV Bi^+ primary ion source (LMIG) as the analysis beam delivering a 1.2 pA current and rastering an area of $100 \times 100 \mu\text{m}^2$, and a 2 keV Cs^+ ion beam as the sputtering beam delivering a 100 nA current and rastering an area of $700 \times 700 \mu\text{m}^2$. Profile acquisitions were performed in negative ion mode because providing higher sensitivity for oxides. Data acquisition and post-processing analysis were performed using the Ion-Spec software. The ion depth profiles were normalised with reference to Al_2^- intensity plateau, corresponding to the alloy substrate. The intensities of all ions were divided by the value of Al_2^- ion intensity (in the plateau region).

SEM images were obtained with a ZEISS Ultra-55 field emission scanning electron microscope (FE-SEM) in standard conditions. A voltage of 10 kV and a pressure inside the chamber less than 2.10^{-5} mbar were used. EDX Analysis were performed on a LEICA S440 emission scanning electron microscope (FEG-SEM) couple with an energy-dispersive X-ray spectroscopy (EDX) detector at the LISE (UMR8235-UPMC/CNRS).

An ICP-OES iCAP 6300 (Thermo Fisher Scientific) was used to measure the concentration of dissolved species in the baths at the end of pre-treatments. This allows us to estimate the surface dissolution rates in the bath. Standards of Al, Cu, Mg from 0.01 ppm to 50 ppm were used to calibrate the instrument. The concentration of dissolved species was normalised to the average of sample area (1.6 cm^2 for 2024-T3 and 2.5 cm^2 for pure aluminium). Front

sides of the samples were mirror polished (as described above) and the back sides were grinded with SiC paper (1200).

3 Results

3.1 Surface morphology

Scanning electron microscopy (SEM) with energy-dispersive X-ray (EDX) spectroscopy have been performed on a polished AA-2024-T3 to investigate the topography and the type of intermetallic particles. SEM images (Fig. 1, A)) of AA-2024-T3 show the presence of many particles with different sizes and shapes. Some holes (dark areas) correspond to particles removed during the polishing. According to EDX and SEM measurements, round-shaped particles with an approximate size of 1 μm are associated to Θ - Al_2Cu and S- Al_2CuMg phases. Bigger particles with irregular shapes correspond to Al-Cu-Fe-Mn-Si phases with an average stoichiometry of $\text{Al}_{21}\text{Cu}_6\text{Fe}_2\text{MnSi}_{0.3}$. X-ray diffraction (XRD) measurements (not presented here) confirmed the presence of Θ - Al_2Cu and S- Al_2CuMg phases. $\text{Al}_7\text{Cu}_2\text{Fe}$ phase was also identified. The Al-Cu-Fe-Mn-Si phase could originate from $\text{Al}_7\text{Cu}_2\text{Fe}$ with manganese substituting iron. Hughes *et al.* [24] have identified 6 phases from different samples of AA-2024-T3, including S-phase, Θ -phase and Al-Cu-Fe-Mn-Si. They evidenced that the various compositions and distributions of more than 3 types of intermetallics can be influenced by aging conditions. Indeed, in our study, the alloy presents many particles with a size below the micrometre but the EDX measurements were performed on particles not smaller than one micrometer. Verdalet-Guardiola [25] also identified disparities of intermetallic particles recovery rates and distribution on three types of 2024-T3 alloys from different suppliers.

Fig. 1, B) presents the EDX image of AA-2024-T3 polished sample. According to the previous analysis, it is possible to observe the Al-Cu, Al-Cu-Mg and Al-Cu-Fe-Mn-Si particles. As shown by the elemental mapping, the particles are randomly distributed. It is noted that copper is the alloy element observed on all particles.

Fig. 1. SEM images of polished AA-2024-T3 alloy observed with secondary electrons (A) and B) EDX images) of a polished 2024-T3 alloy.

Fig. 2 presents SEM secondary electrons images of AA-2024-T3 samples surface after pre-treatments A-C) nitric acid, D-H) sulphuric acid and I-L) mixture of nitric and sulphuric acids. At lower magnification (Fig. 2, A), D) and I)), SEM images show modifications of the intermetallic particles and the matrix with presence of several holes resulting from the removal of intermetallic particles induced by different pre-treatments. The remnant intermetallic particles (light colour) present various shapes, sizes and textures. As described above (Fig. 1), the round-shaped particles of 1 μm in size correspond to θ-Al₂Cu and S-

Al₂CuMg phases, whereas the irregular in shape and bigger particles to Al-Cu-Fe-Mn-Si. The Al-Cu-Fe-Mn-Si particles are easily recognized, and detailed analyses on these particles were performed.

Most of intermetallic particles seem not to be attacked during pre-treatment in nitric acid (Fig. 2, A) and B)). Only smaller particles, associated to Θ -Al₂Cu and S-Al₂CuMg, seem to be attacked. Some of them have been removed (dark holes), and some of them have been partially attacked and present a spongy texture (Fig. 2, C)). Particles with this spongy texture are composed of a continuous solid phase remnant network and many nanosized pores [26]. This phenomenon already observed for the 2024-T3 alloy after 15 min treatment in 2.8 M HNO₃ bath [27] is known as dealloying. This was also evidenced for Al(Cu,Mg) phase in the case of AA-2024-T3 after oxidising acid pickling in Turgo Smut Go NC by Alba-Galvin *et al.* [17]. This type of morphology results from the preferential dissolution of aluminium, and magnesium in the case of S-phase. Two phenomena can be distinguished: either copper enrichment of the particle which becomes more cathodic, or small copper particles detachment from intermetallic copper, which create an electrochemical cell surrounding the S-phase. It leads to the dissolution of surrounding matrix in both cases, called trenching [19,28,29].

After a pre-treatment in sulphuric acid, (Fig. 2, E-G)), more dealloyed particles are observed than after the pre-treatment in nitric acid (Fig. 2, D)). Concerning dealloyed particles, some particles are completely dealloyed and the matrix is dissolved around the particles, some particles are only attacked in their centre.

In the mixture of both acids (nitric and sulphuric), the alloy surface appears more attacked (Fig. 2, I)) showing holes with entirely or partially removed particles. All remnant particles

are dealloyed and some of them present a kind of light mist (Fig. 2, K)). In attacked large and irregular particles, the continuous solid phase remnant network and pores (Fig. 2, L)) are more significant than after pre-treatment in sulphuric acid ((Fig. 2, H)). These particles are likely Al-Cu-Fe-Mn-Si particles according to their sizes and irregular shapes.

EDX measurements were performed on the sample pre-treated in 150 g/L H₂SO₄ and 100 g/L HNO₃. Results are presented in Fig. 3. According to the shape, size and constituents, these dealloyed particles seem to be Al-Cu-Fe-Mn-Si-type particles. The analysis performed on dealloyed areas showed copper rich-areas with copper/aluminium ratio of 0.9 and 0.6 for areas 1 and 2, respectively. A second analysis performed on a particle partially attacked showed that the dealloyed area (area 3) contains more copper than the intact area (area 4). These EDX analyses confirm the copper enrichment of dealloyed particles due to preferential dissolution.

It can be concluded that different samples morphologies were identified depending on acids treatments. The sample pretreated in mixture of acids seems the most modified with many removed and/or dealloyed particles. Moreover, the size of continuous solid phase remnant networks of the dealloyed particles was shown to be dependent on the pre-treatment conditions. Hashimoto *et al.* [26] studied the dealloying phenomenon of S and θ phases in 1.5 M NaCl media, and they demonstrated the gradual evolution of pore size and a continuous formation of solid phase remnant network during dealloying. From nanosized pores and a relatively fine remnant at the beginning, it evolves to relatively large pores and a coarser-remnant network. This could mean the beginning state of dealloying for the sample pretreated in sulphuric acid whereas the more severe attack can be observed for the sample pretreated in mixture of acids. Moreover, authors highlighted the presence of copper

nanoparticle at the intersection of remnant branches of dealloyed particles and these particles were covered of 2 nm thick copper film. Qi *et al.* [30] also showed the crystallization of Cu (111), (2000), (220) and (311) on the surface of a dealloyed Al-Cu alloy after immersion in HCl media at 90°C during a few hours.

Fig. 2. SEM images of AA-2024-T3 alloy after pre-treatments in A-C) 100g/L nitric acid, D-H) 150 g/L sulphuric acid and I-L) mixture of 150 g/L sulphuric acid and 100 g/L nitric acid observed by SEM (secondary electrons, 10 kV).

	At%	Area 1	Area 2	Area 3	Area 4
	Aluminium	47	55	69	78
	Copper	44	35	29	9
	Iron	6	7	1	10
	Manganese	3	4	1	3

Fig. 3. EDX measurements (and SEM backscattered electrons at a voltage of 15 kV) of the AA-2024-T3 sample pre-treated in a mixture of 150 g/L sulphuric acid and 100 g/L nitric acid.

3.2 In-depth chemical characterisation by ToF-SIMS

Chemical surface and in-depth characterisations were performed by ToF-SIMS ion depth profiling. The ToF-SIMS ion depth profiles for a polished AA-2024-T3 sample are presented in Fig. 4. The intensity of ion signals is reported in logarithmic scale. Although ToF-SIMS is not directly quantitative, signal intensity changes with sputtering time reflect in-depth concentration variations. Observing the intensity changes of different ions with sputtering time, three different regions can be identified in the in- depth profile: oxide layer, oxide/metal interfacial zone and the metallic substrate.

The first one, corresponding to the first 35 s of sputtering, is characterized by the maximum intensity of AlO_2^- ($m=58.98$ amu) signal whereas the Al_2^- ($m=53.96$ amu) and Cu^- ($m=62.93$ amu) signals, characteristic of the metal, remains low. This region is associated to the oxide layer, which is mainly composed of oxidized aluminium. The second region starts with the decrease of the AlO_2^- signal intensity, which corresponds to the increase of Al_2^- , CuO^-

($m=78.92$ u) and Cu^- signals. After 35 s, the maximum intensity of CuO^- and Cu^- (markers of copper hydroxide/oxide and metallic copper, respectively [31]) are reached and the Al_2^- is still increasing. This suggests an interfacial region rich in copper, due to the presence of Cu-rich intermetallic particles located at the interface between metal and oxide. This region, that extends from 35 s to 85 s, corresponds to both the oxide and metallic substrate as the roughness of the sample is significant, as already discussed previously [4,32,33]. In this region, the CuO^- signal shows a maximum of intensity at 45 s, whereas the maximum intensity of Cu^- signal is observed 5 s later (at 50 s). Despite the complex effect of sample roughness, which can influence the shape of ion profiles in the interfacial region, the slow decay of CuO^- signal, that follows the trend of Cu^- signal, indicates the presence of copper oxide at the periphery of Cu-rich intermetallic particles. This was previously evidenced by Cornette *et al.* [31]. The presence of copper oxide on intermetallic particles is not expected from thermodynamics, which predicts a preferential growth of an aluminium oxide as long as the intermetallic particle contains sufficient metallic aluminium. The presence of copper oxide would mean that preferential oxidation of aluminium on the intermetallic surface leads to complete depletion of aluminium, so that then copper oxidation becomes possible at the intermetallic particle surface. The MgO^- signal also reaches its maximum intensity at around 50 s, indicating that magnesium oxide is located close to the interface. Then, the last, third region after 85 s, characterised by the of Al_2^- intensity plateau corresponds to the metallic substrate. Summarizing, the alloy is covered by an aluminium oxide and is enriched in copper at the metal/oxide interface due to the oxidation process of intermetallic particles. Similar profiles have been observed previously [4,31,32,34].

Fig. 4. ToF-SIMS ion depth profiles recorded for a mirror polished AA-2024-T3 alloy.

A comparison of the in-depth profiles for polished sample and pretreated samples in sulphuric acid (Fig. 5, A)) and in nitric acid and a mixture of acids (Fig. 5, B)) is shown in Fig. 5. The time to reach the interfacial zone is longer for the samples immersed in sulphuric acid (50 s) and in the mixture of acids (45 s) than for the polished sample (35 s as presented in Fig. 4). The sputtering time to reach the substrate is longer for all pretreated samples, especially after the treatment in the mixture of acids (150 s). Assuming the same sputtering yield for all samples (as the composition of the oxide scales is similar), the data indicate that slightly thicker oxide layers are present on pretreated samples. However, the slower stabilization of Al_2^- signal to its maximum intensity (plateau) can also be induced by a higher roughness of pretreated samples.

Concerning copper species, the Cu^- signal reaches its maximum intensity in the interfacial zone as for the polished sample. The maximum signal intensities are 10 times higher after immersion in acid baths. This is characteristic of a copper enrichment induced by the pre-treatments. Similarly to our findings, the copper enrichment at the oxide/metal interface of AA-2024-T3 was already observed by XPS depth profiles by Vander *et al.* [22] after a

Sanchem pre-treatment (phosphate cleaner with no silicate bath then sodium bromate in nitric acid bath). Using TEM, Liu *et al.* [23] evidenced the presence of 1 nm thick copper enrichment underlying the alloy region for Al-Cu magnetron sputtered alloy immersed in nitric acid. For the sample immersed in sulphuric acid (Fig. 5, A), a high CuO^- signal intensity spreads through the whole oxide region. Moreover, the Cu^- signal increases quickly from the firsts 5 s of sputtering to reach its maximum intensity close to the metal/oxide interface. The intense CuO^- and Cu^- signals through the oxide layer can be explained by the dissolution of Cu-rich intermetallic particles then the redeposition of metallic copper over the surface, which subsequently undergoes the oxidation. The copper redeposition was also evidenced by Buchheit *et al.* [29] and Viroulaud [35]. Zhou *et al.* [36] and Liu *et al.* [37] demonstrated the incorporation copper into the oxide film as oxidized species and nanoparticles which subsequently oxidized. The maximum intensity of Cu^- in the interfacial zone indicates a copper enrichment at the metal/oxide interface.

In order to compare Cu enrichment in different samples, the $\frac{\text{Cu}^-}{\text{Al}_2^-}$ signal ratios have been plotted (Fig. 6). The differences are visible in the first 75 seconds of sputtering showing the copper enrichment in the oxide and interfacial zones. The polished sample shows the lowest ratio, the sulphuric acid treatment leads to the highest $\frac{\text{Cu}^-}{\text{Al}_2^-}$ ratio.

Fig. 5. Comparison of ToF-SIMS ion depth profiles for A) polished sample and sample pretreated in sulphuric acid, B) samples pretreated in nitric acid and a mixture of nitric and sulphuric acids.

Fig. 6. Comparison of $\frac{Cu^-}{Al_2^-}$ ratios for polished and pretreated samples.

3.3 Chemical analysis of surfaces by XPS

The surface chemical analysis of all samples before and after pre-treatment was performed by XPS. High-resolution Al 2s, Cu 2p and Cu LMN spectra have been used to obtain the surface composition and to estimate the copper enrichment induced by pre-treatments. The results for the polished sample and HNO₃ pre-treated sample are presented in Fig. 7. The carbon, not shown here, is attributed to surface contamination. The position of the C-C bond

is 286.1 ± 0.1 eV and 286.2 ± 0.1 eV for polished sample and pre-treated in HNO_3 , respectively. The nonconductive oxide layer above metallic aluminium is responsible of the C-C shift to higher binding energy than the 285 eV position expected for C-C bonds. The overlap of Al 2p and Cu 3p peaks prevents using Al 2p core level for quantitative analysis. Al 2s spectra are fitted with peaks corresponding to the metallic aluminium at 118 ± 0.1 eV and Al(III) oxide/hydroxide at 120.6 ± 0.2 eV (Fig. 7, A) and B)) [38]. Cu 3s appears in the binding energy range of Al 2s core level spectrum at 123.1 ± 0.2 eV. Al(III) and Al(0) peaks (Fig. 7, B)), associated to aluminium oxide and metal, respectively, show a similar intensity ratio indicating no significant modifications in the oxide layer thickness. However, an increase of Cu 3s signal observed after pre-treatment in nitric acid indicates a copper enrichment.

The analysis of Cu 2p and Cu LMN spectra presented hereafter allows us to determine the chemical state of copper. For the polished sample, three components are present in the Cu $2p_{3/2}$ core level region (Fig. 7, C)): at 932.6 ± 0.1 eV, 933.6 ± 0.2 eV, and 934.8 ± 0.1 eV. The first peak at 932.6 ± 0.1 is attributed to Cu(I) and Cu(0) [39,40]. The presence of copper metal and oxide has been confirmed by the analysis of Auger Cu LMN line (Fig. 7, E)) discussed below. The second peak at 933.6 ± 0.2 eV can be associated to metallic copper in the intermetallic particles. For pure metallic copper, the Cu $2p_{3/2}$ peak is expected at 932.6 ± 0.1 eV [39,40] but according to previous observations the bimetallic systems show often positive shifts of one or both metallic peaks due to modifications of electronic structure of the bimetallic system with reference to the pure metal. Son *et al.* [41] observed Cu $2p_{3/2}$ at 933.6 eV on a metallic thin film of Al_2Cu , thus presenting a shift of 1 eV compared to pure Cu. This effect was also observed in other published works. Liu *et al.* [42] showed the higher binding energy peak at 933.8 eV for magnetron-sputtered Al-33%Cu alloy, which was attributed to the metallic copper present in CuAl_2 phase. Similarly, Pashusky *et al.* [43] also

reported that the increase of Cu in Cu-Al(100) leads to a progressive shift of Cu 2p_{3/2} peak to higher binding energies up to 933.2 eV. In order to confirm the effect of Cu alloying to Al and the resulting binding energy shift, a pure metallic Θ -Al₂Cu phase was analysed here. The details will be reported in a separate, forthcoming paper. The results confirm the shift of metallic Cu 2p_{3/2} peak to 933.5 eV induced by alloying with Al. Moreover, the calculated modified Auger parameter (1851.4 eV) for a pure Θ -Al₂Cu intermetallic sample is slightly higher than for pure metallic copper (1851.2 eV) [39,40]. The third Cu 2p_{3/2} peak at 934.8 ± 0.1 eV is associated to the Cu(II) mainly in hydroxide state [39,40]. The absence of detectable satellite characteristic of Cu(II) at higher binding energy can be explained by the small amount of Cu(II).

In order to get more information about the chemical state of copper the analysis of Cu LMM Auger spectra was performed on polished and pre-treated samples (Fig. 7, E) and F), respectively). For the polished sample (Fig. 7, E)), Cu LMN shows a metallic component at 918.1 ± 0.1 eV and a second component at 916.2 ± 0.1 eV corresponding to copper oxide or hydroxide, in agreement with previous results [31,44]. This fitting was performed by using the Auger line obtained previously for model reference samples (pure metallic copper and copper oxide).

The Cu 2p_{3/2} fitting for the sample immersed in nitric acid shows a high intensity peak at 933.7 ± 0.1 eV related to Cu(0) in the intermetallic particles (Fig. 7, D)) and a low intensity peak at 932.7 ± 0.1 eV associated to pure Cu(0) due to strong copper enrichment and/or Cu(I). The Cu LMN (Fig. 7, F)) shows only a metallic component at 918.0 ± 0.1 eV allowing us to assign the peak at 932.7 eV to metallic Cu.

Fig. 7. XPS A) Al 2s, C) Cu 2p_{3/2} and E) Cu LMN high resolution spectra of AA-2024-T3 mirror polished and XPS B) Al 2s, D) Cu 2p_{3/2} and F) Cu LMN high resolution spectra of AA-2024-T3 pretreated in 100 g/L HNO₃ at 50 °C during 10 min.

Similar peak fittings were performed for XPS data obtained for samples pre-treated in sulphuric acid or in the mixture of acids and the results are presented in supplementary

information in **Erreur ! Source du renvoi introuvable.** The Cu 2p_{3/2} peak shape is similar for the samples pre-treated in sulphuric acid and the polished sample, whereas for samples pre-treated in the mixture of nitric and sulphuric acids is similar to the samples pre-treated in nitric acid.

The calculated oxide thickness is in the same range for all samples: 2.8 ± 0.3 nm after polishing, 3.0 ± 0.3 nm after the pre-treatment in 100 g/L nitric acid, 3.2 ± 0.3 nm after pre-treatment in 150 g/L sulphuric acid, and 3.0 ± 0.3 nm after pre-treatment in the mixture of acids. The oxide thickness was calculated using equation S1 (shown in the supplementary information).

The chemical compositions of samples after polishing and after different treatments are displayed in Table 1. A copper enrichment is observed after all pre-treatments. The sulphuric acid bath led to the highest copper content with almost 5 at.%. The pre-treatments seem to slightly increase the magnesium content. The analysis of Mg 1s spectra showed one peak assigned to Mg (II).

Table 1. Surface composition (in atomic and weight percentage) calculated from XPS data (processed with AvantageTM software).

	At %			Wt %		
	%Al	%Cu	%Mg	%Al	%Cu	%Mg
Polished	99.0 ± 0.5	0.6 ± 0.5	0.3 ± 0.5	98.3 ± 0.5	1.4 ± 0.5	0.3 ± 0.5
H ₂ SO ₄	94.3 ± 0.5	5.1 ± 0.5	0.6 ± 0.5	88.3 ± 0.5	11.2 ± 0.5	0.5 ± 0.5
HNO ₃	96.4 ± 0.5	2.6 ± 0.5	1.1 ± 0.5	93.2 ± 0.5	5.9 ± 0.5	0.9 ± 0.5
Mixture	95.8 ± 0.5	2.3 ± 0.5	1.2 ± 0.5	93.6 ± 0.5	5.4 ± 0.5	1.0 ± 0.5

In order to better understand the evolution of the chemical environment as a function of pre-treatment conditions a copper indicator based on the XPS data was used. The Cu XPS indicator takes into account the attenuation of metallic signal intensities due to the presence of oxide layer on the extreme surface according to equation 1. The Cu XPS indicator is the ratio between the intensity of metallic or oxidised copper peak and the intensity of metallic aluminium according to the following formula [eq 1]:

$$Cu\ XPS\ indicator = \frac{\frac{I_{Cu}}{\exp\left(-\frac{d}{\lambda_{Cu}^{Al_2O_3}}\right)}}{\frac{I_{Al(0)2s}}{\exp\left(-\frac{d}{\lambda_{Al}^{Al_2O_3}}\right)}} \quad [equation\ 1]$$

The calculations made for the three components of the Cu 2p_{3/2} peak are shown in Fig. 8. After all pre-treatments, a significant increase has been noted for the Cu(0) associated to intermetallic particles. It is well known that selective dissolution of aluminium and Cu enrichment occurs during pre-treatments leading to dealloying of Cu-rich intermetallic particles [17,26]. This can explain the increase of Cu-related signals more significant for the sample pre-treated in sulphuric acid. A small increase of the Cu(0)/Cu(I) indicator is observed after pre-treatment in nitric acid and the mixture of acids and much more in sulphuric acid. One possible explanation is the accumulation of metallic copper nanoparticles at the intersection of remnant branches of dealloyed particles and the formation of a copper film as observed by SEM, which covered the dealloyed particle surface [26,30]. The other explanation is the copper release, followed by a copper redeposition on the surface during pre-treatment. This phenomenon was already proposed by Buchheit *et al.* [29], who

suggested that dealloying of S-Al₂Cu could provide mobile copper particles, which can be redistributed across the surface. Viroulaud *et al.* [35] have also proposed the hypothesis of copper nanoparticles deposition by reduction of Cu²⁺ present in the solution originating from copper-rich intermetallic particles dissolved during acid pickling step in a bath containing ferric sulphate, nitric acid and sodium bifluoride. The presence of a small amount of Cu(I) cannot be ruled out even if it is unlikely for HNO₃ and acid mixture treated samples because no oxide signal is detected on the Cu Auger peak.

Fig. 8. XPS indicator for the Cu species calculated using [equation 2] before and after pre-treatment in nitric and sulphuric acid baths. The metallic copper associated to intermetallic particles is in red, the pure metallic copper or Cu(I) is in fuchsia and the Cu(II) in blue.

3.4 Analysis of pre-treatment baths by ICP-OES

After the alloy pre-treatments, the used pre-treatment baths were analysed by ICP-OES to measure the weight concentration of aluminium and the two main alloying elements, Cu and Mg. The concentrations of Al after 10 min immersion in the sulphuric acid, nitric acid and mixture of acids baths were 0.8 ± 0.3 ppm, 2.1 ± 0.3 ppm and 2.8 ± 0.2 ppm, respectively. It can be concluded that the sulphuric acid bath is the least aggressive pre-treatment, leading to the lowest dissolution of Al.

The Al concentration was used to determine the dissolution rate of the alloy. In a first approach, the hypothesis of a homogeneous (congruent) dissolution of the metallic surface was made. The molar density of Al in metal, 0.1 mol/cm^3 , was used for the calculations. Results are presented in Fig. 9. The dissolution rate in the sulphuric acid, nitric acid and mixture of acids baths were $14 \pm 6 \text{ nm/min}$, $37 \pm 6 \text{ nm/min}$ and $49 \pm 6 \text{ nm/min}$, respectively. The dissolution rate in the mixture of acids is in the same range ($51 \pm 4 \text{ nm/min}$) as for the commercial Socosurf bath ($\text{HNO}_3\text{-H}_2\text{SO}_4\text{-Fe(III)}$) based deoxidizer), which was studied by Verdalet-Guardiola [25]. Dissolution rates of 2024-T3 can be compared to the ones on pure aluminium (in red) in Figure 10. The dissolution rates of 2024-T3 and pure aluminium are in the same range for each bath. Moreover, the dissolution rate seems to follow the same evolution with bath composition. The dissolution rate is lower in sulphuric acid and higher in nitric acid and mixture of acids. The presence of alloying elements does not seem to affect significantly the dissolution rate of samples in the pre-treatment baths.

Fig. 9. Dissolution-rate of AA-2024-T3 (black) and pure aluminium (red) in H_2SO_4 , HNO_3 and mixture of the two acids (measured by ICP-OES).

To compare the effect of pre-treatments on the main alloying elements (Cu and Mg), the bath composition after pre-treatment was calculated from the element concentrations

measured by ICP-OES. To compare the results with the composition of the alloy, the contents in Cu and Mg were taken as 3.9 – 5.0 wt% Cu, 1.2 – 1.8 wt% Mg and the rest of aluminium in the bulk alloy. Results are reported in Table 2.

The sulphuric acid bath stands out from the other baths. It has the lowest copper content, 0.6 ± 0.5 wt%, which is lower than the Cu content in the alloy bulk (3.9 wt% Cu). This very low amount of dissolved Cu could be explained by a preferential dissolution of Al and Mg or a redeposition of Cu on the alloy surface during pre-treatment. The nitric acid and acid mixture baths have similar copper content, with 4.3 ± 0.5 wt% and 4.2 ± 0.5 wt%, respectively. These contents are close to the Cu content in the alloy but the quantity of dissolved Cu is considerably increased in the nitric acid and acid mixture with respect to the sulphuric acid bath. This is in agreement with the Cu enrichment on the AA-2024-T3 surface measured by XPS after immersion in the sulphuric acid bath.

For Mg, the sulphuric acid treatment leads to a significant Mg enrichment in the bath, 7.0 ± 0.9 wt%, with respect to the Mg content in the alloy (1.2-1.8 wt% Mg). The pre-treatments in the nitric and acid mixture baths give lower Mg amounts of 3.0 ± 0.9 and 2.3 ± 0.9 wt%, respectively, however these values are also higher than the Mg content in the bulk alloy. Thus Mg seems preferentially dissolved in the pre-treatment bath, particularly in the sulphuric acid bath. This is in agreement with the lower Mg concentration measured by XPS on the AA-2024-T3 surface after immersion in the sulphuric acid bath.

Table 2. Amounts of Al, Cu, Mg (in weight percent) dissolved in the pre-treatment baths (measured by ICP-OES) and on the surface (measured by XPS).

		% Al	%Cu	%Mg
Alloy composition		REST	3.9 – 5.0	1.2-1.8
Dissolved species in the baths measured by ICP-OES	H ₂ SO ₄		0.6 ± 0.5	7.0 ± 0.9
	HNO ₃		4.3 ± 0.5	3.0 ± 0.9
	Mixture		4.2 ± 0.5	2.3 ± 0.9
Surface composition measured by XPS	Polished		1.4 ± 0.5	0.3 ± 0.5
	H ₂ SO ₄		11.2 ± 0.5	0.5 ± 0.5
	HNO ₃		5.9 ± 0.5	0.9 ± 0.5
	Mixture		5.4 ± 0.5	1.0 ± 0.5

4 Discussion

The pre-treatment in acid solutions leads to surface modifications such as the scalloped surface [18] and the dissolution/removal of intermetallic particles. Deoxidizing in a mixture of 150 g/L H₂SO₄ and 100 g/L HNO₃ gives the most attacked surface with a high surface fraction corresponding to defects and holes where all remaining particles are dealloyed. This high density of holes leads to an increase of the surface roughness resulting in less sharp oxide/metal interface. Increased sputtering times in ToF-SIMS in-depth profiles reflect this roughening. The higher dissolution rate of 49 ± 6 nm/min in the acid mixture was also revealed by ICP-OES analysis. The sulphuric acid bath was less aggressive, giving a dissolution rate about 14 ± 6 nm/min. However, dissolution/removal of intermetallic particles was also observed.

Regarding the influence of acid treatment on alloying elements, it should be noted that the sulphuric acid solution led to the highest concentration of dissolved magnesium as shown by

ICP-OES, whereas few differences were observed on pre-treated samples by XPS and ToF-SIMS. It is interesting to note that the Mg amount in the bath was superior to the initial content of Mg in the alloy. This may be explained by a different dissolution rate of the sides of the samples, with different surface finishing, one side was mirror polished and the other one grinded with SiC paper 1200.

Significant differences related to pre-treatments with different acids were observed for copper. As expected and reported in previous studies [4,12,20–23], surface copper enrichment was clearly evidenced here by XPS and ToF-SIMS. The highest copper content was observed for the sample pre-treated in the sulphuric acid bath.

A metallic copper enrichment at the interface between oxide and metallic substrate after pre-treatments was clearly observed by ToF-SIMS, in agreement with previous studies [22,23]. XPS analyses demonstrated an enrichment in Cu(0) associated to intermetallic particles, which can be explained by the preferential dissolution in favour of copper (dealloying of intermetallic particles) and/or the revealing of new intermetallic particles due to the dissolution of the matrix.

The distribution of copper in the oxide layer is different after the immersion in sulphuric acid with respect to the mixture of acids and the nitric acid. For the sample immersed in sulphuric acid, ToF-SIMS measurements showed that copper is homogeneously distributed within the entire oxide layer compared to the polished sample. XPS also confirmed the presence of copper oxide. On the samples pre-treated in HNO_3 and $\text{HNO}_3/\text{H}_2\text{SO}_4$, no copper was detected in the oxide layer by ToF-SIMS. Moreover, the Auger signature from Cu LMN XPS spectra confirmed that copper was in the metallic state.

The copper enrichment could be explained in different ways. Firstly, the metallic copper enrichment on intermetallic particles can be discussed. The common effect of studied pre-treatments is the metallic copper enrichment at the metal/oxide interface. In the AA-2024-T3, Cu is present in the intermetallic particles. EDX analyses (Fig. 3) revealed the copper enrichment on dealloyed areas of intermetallic particles. The Cu enrichment can be explained by the preferential dissolution in favour of copper (dealloying of intermetallic particles). Tardelli *et al.* [45] already observed this dealloying phenomena and a copper enrichment on Al_2Cu , Al_2CuMg and Al-Cu-Fe-Mn-Si phase samples after 50 hours of immersion in 200 g/L H_2SO_4 . For the Al_2Cu sample [45], it was attributed to the formation of a compact copper film at the surface. For the Al_2CuMg and Al-Cu-Fe-Mn-Si samples [45], the formation of copper nodules (around 50 nm) at the surface was shown. Even for a low content of copper in the Al-Cu-Fe-Mn-Si, the dissolution of Al, Si, Fe and Mn led to copper enrichment and the formation of a porous film [45].

Another hypothesis concerning the presence of pure copper can be proposed. The higher intensity of Cu(0) and/or Cu(I) XPS signal (Fig. 8) after pre-treatment suggests the presence of pure metallic copper. This could be explained by accumulation of copper at the intersection of remnant branches of dealloyed areas [26] and the formation of a copper film covering the dealloyed particles [45].

A redeposition/redistribution of copper over the surface due to the reduction of mobile Cu^{2+} for the sample immersed in H_2SO_4 [29,35] can also be envisaged. ToF-SIMS in-depth profiles revealed the copper enrichment in the entire oxide layer compared to the polished sample. XPS analysis on this sample (Fig. 8) showed an increase of Cu(II) and a considerable increase of pure Cu(0) and/or Cu(I). ICP-OES analysis revealed a very low dissolution of Cu during pre-

treatment, giving less Cu than in the bulk alloy. This is in accordance with ToF-SIMS and XPS results, which showed the highest copper enrichment after pre-treatment in sulphuric acid (Table 2). These results lead to the conclusion that copper is redeposited during pre-treatment in sulphuric acid. The redeposited copper is subsequently oxidized explaining the presence of copper oxide in the oxide layer.

The Cu redeposition has been previously reported by Buchheit *et al.* [29] and Viroulaud *et al.* [35]. Campestrini *et al.* [46] showed the influence of this Cu on the subsequent steps of alloy treatment. They reported the presence of copper or copper oxide nodule deposits after deoxidizing in sulphuric/phosphoric bath inhibiting the growth of the chromate film above the matrix.

5 Conclusions

The AA-2024-T3 alloy has been characterized by SEM, XPS and ToF-SIMS after deoxidizing in sulphuric acid, nitric acid, and a mixture of both acids. Baths were also characterised by ICP-OES. The most important conclusions of the influence of the acid treatment on the surface chemical composition are the following:

- No significant evolution of the oxide thickness was observed after pre-treatment
- The common effect of the studied deoxidizers is copper enrichment at the metal/oxide interface. The highest copper enrichment was observed for H₂SO₄ bath. Metallic copper was observed at the metal/oxide interface and copper oxide in the entire oxide layer.
- The HNO₃ and HNO₃/H₂SO₄ baths led to the metallic copper enrichment and different surface morphologies. With HNO₃/H₂SO₄, all intermetallic particles were

dealloyed and many of them were removed whereas for HNO_3 bath, only the Al_2Cu and Al_2CuMg particles were attacked and bigger particles remained intact.

- Copper enrichment was principally attributed to dealloying of intermetallic particles, resulting in formation of Cu-rich remnant, according to the EDX and XPS measurements. In the case of H_2SO_4 deoxidizer, it could also be attributed to the copper redeposition as concluded from ICP-OES analyses.

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