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Power ultrasound irradiation during the alkaline etching process of the 2024 aluminum alloy

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ABSTRACT

Prior to any surface treatment on an aluminum alloy, a surface preparation is necessary. This commonly consists in performing an alkaline etching followed by acid deoxidizing. In this work, the use of power ultrasound irradiation during the etching step on the 2024 aluminum alloy was studied. The etching rate was estimated by weight loss, and the alkaline film formed during the etching step was characterized by glow discharge optical emission spectrometry (GDOES) and scanning electron microscope (SEM). The benefit of power ultrasound during the etching step was confirmed by pitting potential measurement in NaCl solution after a post-treatment (anodizing).

1. Introduction

Aluminum 2024 is an aluminum alloy with copper as primary alloying element. Due to its interesting mechanical properties, i.e. high strength and good fatigue resistance, the 2024 aluminum alloy is widely present in aerospace industries and particularly in aircraft structures (wings and fuselage) [1]. The metals are alloyed to increase strength by forming intermetallic particles. For the 2024 aluminum alloy, two main types of intermetallic particles could be identified: Al–Cu–Mg and Al–Cu–Fe–Mn particles. Al–Cu–Mg particles are anodic compared to the aluminum matrix and have a relatively round shape. Al–Cu–Fe–Mn particles have an irregular shape and are cathodic compared to the Al matrix. The behavior of 2024 aluminum alloy intermetallic particles was already studied in many papers, because if their presence increases the mechanical properties [1], their particular microstructure contributes to a poor resistance of the 2024 aluminum alloy [2]. In fact, these intermetallic particles increase the susceptibility of this alloy to localized corrosion [3,4] and induce galvanic coupling phenomena [5]. Post-treatments (anodizing or conversion coating) are generally carried out to improve corrosion resistance of the 2024 aluminum alloy [6–8]. Moreover, surface preparation efficiency is essential to obtain good corrosion resistance of post-treatments [9,10].

Prior to anodizing or conversion coating, aluminum alloy substrates are cleaned in a series of several steps combining etching, deoxidizing/desmutting and rinsing. The aim of surface preparation is to remove surface contaminants, natural oxide and intermetallic particles present at the aluminum alloy surface [10]. This work focuses on the etching step. Sodium hydroxide solution is frequently used [11,12]. Etching temperature and immersion time constitute process parameters that strongly affect the final surface properties of aluminum alloys [13].

On another hand, use of ultrasound is commonly used for cleaning in surface treatment industries, since it is a good way to remove dirt without damaging the products [14–16]. In fact, ultrasound is known to induce cavitation phenomena in liquid media, and some of the bubbles generated collapse asymmetrically near the surface. Thus, a mechanical cleaning effect is induced due to the high velocity fluid jet delivered while the bubbles collapse, associated with a global stirring effect in the liquid media [17]. Large-scale equipment is possible as shown by recent developments in the field of ship hull cleaning [14], but the heterogeneity of the acoustic field [18] induces a distribution of the power, which needs to be evaluated [17]. Visualization of the actives zones by laser tomography reveals noticeable differences when an obstacle in placed is the propagation field, to be taken into account in the sample positioning [19].

In this study, effects of power ultrasound irradiation (20 kHz, 70 W measured using the calorimetric method) during alkaline etching were investigated for the 2024 aluminum alloy, at two different temperatures (25 and 50 °C) and for different immersion times. The etching rate was determined, and the alkaline layer

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Table 1
Composition of the 2024 aluminum alloy (wt%).

Alloy	Cu	Mg	Fe	Mn	Si	Al
2024	4.5	2.0	0.5	0.8	0.8	Bal.

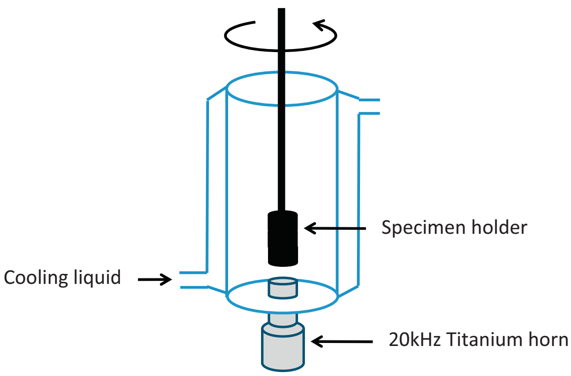

Fig. 1. Equipment for the etching process under power ultrasound irradiation.

formed during the etching step was characterized (composition, thickness and morphology). The efficiency of alkaline etching under ultrasound presence was also examined after deoxidizing in acid solution. The corrosion resistance of a post-treatment (anodizing) after various pre-treatment with or without ultrasound was also tested thanks to pitting potentials measurement.

2. Experimental

2.1. 2024 Aluminum alloy treatments

A circular electrode, 25 mm in diameter and made of a 2024-T3 Al alloy, was used. Its chemical composition is given in Table 1. The aluminum alloy was cleaned in ethanol before use. The etching step was applied in NaOH solution at a concentration of 50 g/L, and operated at 25 and 50 °C, from 30 s to 5 min. Experiments were carried out in a jacketed glass cylindrical vessel (diameter: 60 mm and height: 130 mm) with temperature control (Fig. 1). Aluminum alloy discs were put into a tailor-made holder acting as an electrode with an active area of 3.14 cm^2. This electrode was stirred at 800 rpm. For experiments under ultrasound irradiation, the holder containing aluminum was opposite the ultrasonic source. The distance between the aluminum electrode and the ultrasonic source was 1 cm. A 25 mm diameter titanium horn at 20 kHz was used as an ultrasonic source to transmit ultrasound to the liquid media (Sonics & Materials, Danbury, USA). The acoustic power, measured by the calorimetric method, was 70 W. After the etching process, all samples were rinsed and dried before characterization.

The deoxidizing step was carried out in nitric acid solution at 30% volume, and operated at 20 °C for 3 min. Samples were rinsed before characterization.

The anodizing post-treatment was performed under 20 V at 20 °C for 10 min, in sulfuric acid solution at a concentration of 180 g/L. Anodic layer thickness is about 5 μm.

2.2. 2024 Aluminum alloy characterization

The etching rate was determined from weight loss [7]. For a sample with an area A (cm^2), a density ρ (g/cm^3), an etching time t (min) and weights $m1$ and $m2$ (g) before and after etching, the etching rate R (μm/h) is given by $R = 6 \times 10^5 \times (m1 - m2)/(A \times \rho \times t)$. Aluminum density is $\rho = 2.8\ g/cm^3$ and active area is $A = 3.14\ cm^2$. In each case, two samples were used to confirm good reproducibility.

Table 2
Etching rate of the 2024 aluminum alloy after 3 min of immersion in NaOH solution.

	25 °C	50 °C
Without ultrasound	25 μm/h	141 μm/h
With ultrasound	36 μm/h	152 μm/h

Aluminum alloy surfaces after the etching step were characterized by glow discharge optical emission spectrometry (GDOES). Samples were analyzed by GDOES immediately after etching process. GDOES combines sputtering and atomic emission to provide the depth profiles. During operation, plasma is generated in the analysis chamber by the voltage applied between the anode and the cathode (the sample) in presence of argon (Ar) under low pressure. Ionized Ar atoms cause sputtering of the sample area. Sputtered atoms excited in plasma rapidly de-excite by emitting photons with characteristic wavelengths. GDOES measurements were taken using a Jobin-Yvon HORIBA GD Profiler instrument with a 4 mm diameter anode, operating after optimization at a pressure of 650 Pa and a power of 30 W. The wavelengths of the spectral lines used were 396 nm (aluminum), 130 nm (oxygen), 383 nm (magnesium) and 224 nm (copper). A quantitative method has been developed to obtain quantitative profiles. The concept of quantitative method is to establish relationships between intensity of elements and composition, between time and thickness [20].

Samples were observed under the scanning electron microscope (SEM) 24 h after pre-treatments. A JEOL JSM model was used.

Electrochemical experiments were performed in 5% NaCl solution at room temperature 24 h after anodizing, with a classical three-electrode cell, in order to evaluate pitting potentials. The anodic layer with a surface of 1 cm^2 was used as the working electrode, in absence of sealing. Saturated calomel electrode (SCE) and platinum (Pt) wire were used as reference and counter electrodes, respectively. Specimens were polarized from the open circuit potential to the anodic direction, at a rate of 1 mV/s. Four replicates for each treatment were examined.

3. Results and discussion

3.1. Etching rate without and with ultrasound irradiation

Etching rate is estimated after 3 min of immersion in alkaline solution with and without ultrasound irradiation at 25 and 50 °C. Data are shown in Table 2. Etching rate is strongly affected by temperature: the values obtained at 50 °C are always significantly higher than at 25 °C. The use of ultrasound slightly increases the etching rate. Values are higher for the etching step with ultrasound than in silent conditions. Thus, aluminum dissolution increased with temperature and when ultrasound was used during alkaline etching. Nevertheless, a synergetic effect can be observed by combining ultrasound and higher temperatures.

3.2. GDOES profiles after immersion in NaOH solution without and with ultrasound irradiation

Due to aluminum dissolution in alkaline medium, an aluminum hydroxide film is formed on the alloy surface, typical of this kind of alkaline etching step [21]. This residual film could be characterized by quantitative GDOES depth profiles [11].

Fig. 2 illustrates GDOES depth profiles of the aluminum alloy after increasing immersion times (30 s, 1 min, 3 min, 5 min) in alkaline solution at 25 °C in silent conditions. The residual film is effectively observed at any time, and contains the alloying elements (Mg and Cu essentially). Incorporation of Mg and Cu into the layer is probably due to activation of alloying elements contained in