



Unveiling the effect of the electrodes area on the corrosion mechanism of a graphite - AA2024-T3 galvanic couple by localised electrochemistry



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ARTICLE INFO

Article history:

Received 1 February 2018

Received in revised form

24 April 2018

Accepted 24 April 2018

Available online 27 April 2018

Keywords:

AA2024-T3

Graphite

Galvanic coupling

Micro-potentiometry

SVET

ABSTRACT

The corrosion mechanism of two AA2024-T3/graphite galvanic couples, with different electrodes area ratio, was studied in 12.00 mM NaCl solution using the Scanning Vibrating Electrode Technique (SVET) and the Scanning Ion-Selective Electrode Technique (SIET). Both techniques were used, quasi-simultaneously, to monitor the current density distribution and the pH associated to the corrosion process occurring in the galvanic couples. The morphological features and the elemental composition of the electrodes' surfaces, after 20 h of immersion, were analysed by Scanning Electron microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDX). The results show that the area of the electrodes in the galvanic couple significantly influences the corrosion mechanism. For the couple, with the highest AA2024/graphite area ratio (M1), both anodic and cathodic processes developed on the alloy surface, resulting in localised corrosion (trenching of the matrix around intermetallics) at the cathodic zones as detected by SVET and SIET. A more generalised anodic dissolution of AA2024 (corrosion of the matrix and grain boundaries) was observed for the sample with the lowest area ratio (M2), however.

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1. Introduction

The use of composite materials in structural components of aircrafts has been progressively increasing to allow weight reduction and to meet the actual energy saving policies [1–3]. The use of Carbon Fibre-Reinforced Polymers (CFRP) creates multi-material junctions that often comprise aluminium alloys [4,5]. These alloys represent around 20 wt% in modern aircraft designs [6]. Moreover, metallic rivets responsible for assembling the composite parts with the Al alloys panels (particularly the AA2024) create an electrical contact between these dissimilar materials. Therefore, since CFRP is much nobler than AA2024, galvanic corrosion is very likely [4,7,8]. Furthermore, the favourable oxygen reduction reaction (ORR) kinetics on graphite are expected to promote the corrosion of the alloy as well [9]. Thus, the understanding of the galvanic corrosion problems between AA2024 and CFRP is a crucial issue towards

implementation of efficient corrosion protection strategies, allowing the wider use of these materials in aeronautical applications.

It is well known that the AA2024 alloy is very susceptible to corrosion in NaCl electrolyte due to its heterogeneous microstructure and presence of inclusions [10–12]. Intermetallic particles (IMPs), such as the Al-Cu and Al-Cu-(Fe,Mn)-containing phases, act as cathodic sites relatively to the Al matrix and can support the ORR [11,13,14]. On the other hand, the most abundant intermetallic phase of AA2024, the S-phase (Al₂CuMg), represents ca. 60% of the precipitates [10] and is less noble than the Al matrix, evidencing anodic behaviour at the early stage of corrosion [11,15]. The corrosion mechanism involves a self-dissolution step (selective dissolution of Al and Mg [16–18]), the S-phase particles becomes progressively richer in Cu and its electrochemical behaviour turns to be more and more cathodic [10,11,14,19]. Therefore, as corrosion proceeds, the overall cathodic nature of the Cu-rich precipitates is responsible for the localised attack of the neighbour passive Al matrix. Some authors have explained that the trenching of the matrix mainly proceeds by an electrochemical mechanism (anodic dissolution of Al) [11,20]; however, others [15,21–23] consider that

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the process is mainly governed by a chemical dissolution process induced by the alkaline environment surrounding the IMPs (cathodic attack). In any case, a secondary effect of the cathodic activity of the remnants is the reduction of Cu ions dissolved in solution over (and around) them, leading to nodular and uneven Cu deposits [10,19,22,23].

Recently, spatially-resolved electrochemical techniques have been able to successfully extract useful information on the corrosion and corrosion inhibition processes at the micro-scale level. In particular, Lamaka and co-workers [24] have combined the Scanning Vibrating Electrode Technique (SVET) with the Scanning Ion-Selective Electrode Technique (SIET, or micro-potentiometry) to quasi-simultaneously assess the local distributions of ionic current density and H^+ over a corroding surface. Since this pioneering work, the use of SVET/SIET quasi-simultaneously has emerged as a powerful tool to comprehend the electrochemical/chemical reactions governing the corrosion mechanism of various systems [25–31].

In the present investigation, SVET and SIET were quasi-simultaneously applied to measure, respectively, the current density and pH distributions associated with the corrosion activity on AA2024/graphite galvanic couples. A graphite foil was used to simulate the cathodic behaviour of the CFRP material (the cathodic response of carbon fibre-based composites in NaCl solution is coincident to that of pure graphite [4,32]). As demonstrated by Bellucci et al. for the galvanic couple Al alloys/GECM (Graphite-Epoxy Composite Materials) [33], the corrosion intensity of the galvanic process depended upon the cathodic area and rate of the corresponding ORR. Therefore, in this work, two different model couples (M1 and M2) having alloy/graphite area ratios of 10 and 1.5, respectively, were assembled and the corrosion process was studied in the 12.00 mM NaCl.

2. Materials and methods

2.1. AA2024/graphite galvanic coupling models

Two model galvanic couples made of AA2024 and graphite were assembled to simulate the galvanic corrosion processes occurring at the AA2024/CFRP interface. The composition by weight of the AA2024-T3 plate (supplied by Q-Lab) was: 4.65% Cu, 1.87% Mg, 0.61% Mn, 0.19% Fe, 0.13% Zn (Si, Cr and Ti < 0.02%), balance Al. This composition was determined by X-ray fluorescence (S1 TURBO_{SD}, Bruker) and represents the average of triplicate measurements. The 1 mm thick AA2024-T3 plate was cut into ~2 mm coupons using a lever guillotine. A few coupons were kept as such, while others were abraded using a drill tool set (Dremel) until obtaining ~0.85 mm diameter rods. Then, these AA2024 rods were cleaned by acetone and ethanol using ultrasonic bath.

The samples were mounted into an epoxy resin mould and consisted on a 0.13 mm thick graphite foil (99.8% pure, Alfa Aesar) in parallel either to the alloy coupon (M1) or to the alloy rod (M2). The graphite foils employed were ~1.5 mm and ~3 mm wide for M1 and M2, respectively. In both cases, the gap of ~1 mm between the two materials (which were not in physical contact) was respected – Fig. 1. The electrical connections were made at the back side of the epoxy holders by means of a graphite conductive adhesive (Alfa Aesar). Prior to the measurements, the analysed surfaces were ground using SiC paper (up to the 4000 grade) followed by ethanol rinse and distilled water washing and then dried with compressed air. The final ratios between the area of AA2024 and that of graphite were 10 and 1.5, respectively for M1 and M2.

2.2. SVET/SIET measurements

To investigate localised processes over the model couples, SVET and micro-potentiometry (SIET) were employed. The equipment and corresponding software were supplied by Applicable Electronics™ and Science Wares™, respectively. SVET/SIET measurements were performed quasi-simultaneously using the procedure described elsewhere [24].

Insulated Pt-Ir probes (MicroProbes™) with a platinum black deposited on the probe tip were employed as microelectrodes for SVET measurements. The probe was vibrated in two perpendicular planes, vertical (Z) and horizontal (X), at frequencies of 124 Hz (Z) and 325 Hz (X), respectively. The probe diameter was 16 μm, the amplitude of vibration was 32 μm (peak to peak) and it was positioned 100 ± 3 μm above the sample surface. Only the data obtained in the vertical plane of vibration (Z) were considered for further analysis.

For the SIET pH measurements, glass capillary micro-electrodes with a tip orifice diameter of 1.8 ± 0.2 μm were used. A pH selective ionophore-based membrane, with extended pH working range, specially developed for corrosion applications, was used [24]. The local pH selective electrode was placed 50 ± 5 μm above the surface. A homemade Ag/AgCl/0.05 M NaCl mini-electrode was used as external reference electrode. Commercial buffer solutions were used for calibration. The Nernstian slope was -56.3 ± 0.5 mV/pH. The reference potential was recorded in the bulk electrolyte before and after each measurement to detect possible potential drifts.

Accurate positioning of pH microelectrode and SVET microprobe was performed using manual micro-manipulators. Both, current density and pH, were recorded on a 36×26 (sample M1) and 31×21 (sample M2) grid in 0.012 M NaCl solution. This solution was chosen for a sake of comparison with previous results obtained with similar galvanic coupling models [34]. Corresponding distributions were recorded every hour. The scanned area was about $3.5 \text{ mm} \times 4.6 \text{ mm}$. Every measurement was performed in triplicate and their reproducibility was attested.

2.3. SEM-EDX analysis

The scanning electron microscopy experiments and the EDX analysis were performed using a Hitachi S2400 at an accelerating voltage of 20 keV or a JEOL 7001F FEG-SEM/EDX at an accelerating voltage of 15 keV. The EDX detector attached to the SEM Hitachi S2400 is a light elements detector, by Bruker (former Rontec, Germany). It is a SDD detector, model XFlash 5010. The EDX detector from the FEG-SEM is a light elements detector, by Oxford (England) model INCA 250. The reproducibility and repeatability were verified for the micrographs here presented.

2.4. Potentiodynamic polarisation curves

Potentiodynamic polarisation measurements were separately performed on a AA2024-T3 (~1 cm²) and on a graphite foil (~7 cm²) in 12.00 mM NaCl solution using an AMETEK Parstat 2273 (Powersuite® software). One coupon of the same alloy plate (Q-lab) employed for the construction of the models was mounted in epoxy resin and its surface was ground with SiC paper (up to the 4000 grade) prior to testing. The electrochemical set-up of the cell comprised either AA2024 or graphite as working electrode, a platinum wire as counter electrode and an Ag/AgCl/KCl_{sat} (+197 mV/SHE) as reference electrode. Both anodic and cathodic polarisation curves were acquired at a scan rate of 0.1 mV s⁻¹, starting from OCP, under aerated conditions. Before starting polarisation tests, it was verified that stable OCP potentials have been reached, which generally took about 40 min. Measurements were repeated

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