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## Galvanic corrosion over World War II aircraft wrecks

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### **Ancient metals in marine environments: corrosion mechanisms and protective treatments**

#### Abstract

Aluminium usually exhibits a better corrosion resistance than other common metals when exposed to outdoor environments. However, wrecks components made of aluminium alloys, particularly Al-Cu alloys, can be strongly affected by corrosion. The observation of different objects from WWII wrecks indicates more significant degradation in the presence of ferrous parts because of galvanic corrosion. The study focused on two WWII aircraft objects recovered from French coasts: a Supermarine Spitfire aircraft wing, found in 1988 at sea less than 3 miles from the coast of Plérin, and an aircraft propeller found offshore near the beach of Fécamp. We investigated the galvanic corrosion effect over these objects and the influence of their Fe/Al areas ratio between the more noble material (usually ferrous alloy) and the less noble material (usually aluminium alloy). This deterioration was severe due to their exposure to the marine environment and the relatively high amount of Cu (3.4 - 4.5 wt. %) in the Al alloys, provoking pitting, intergranular, and exfoliation corrosion. This study aims to help understanding active corrosion on aircraft wrecks, with the final aim to improve their conservation.

Keywords: WWII cultural heritage; Aluminium alloy; Oxygen consumption.

## **Introduction**

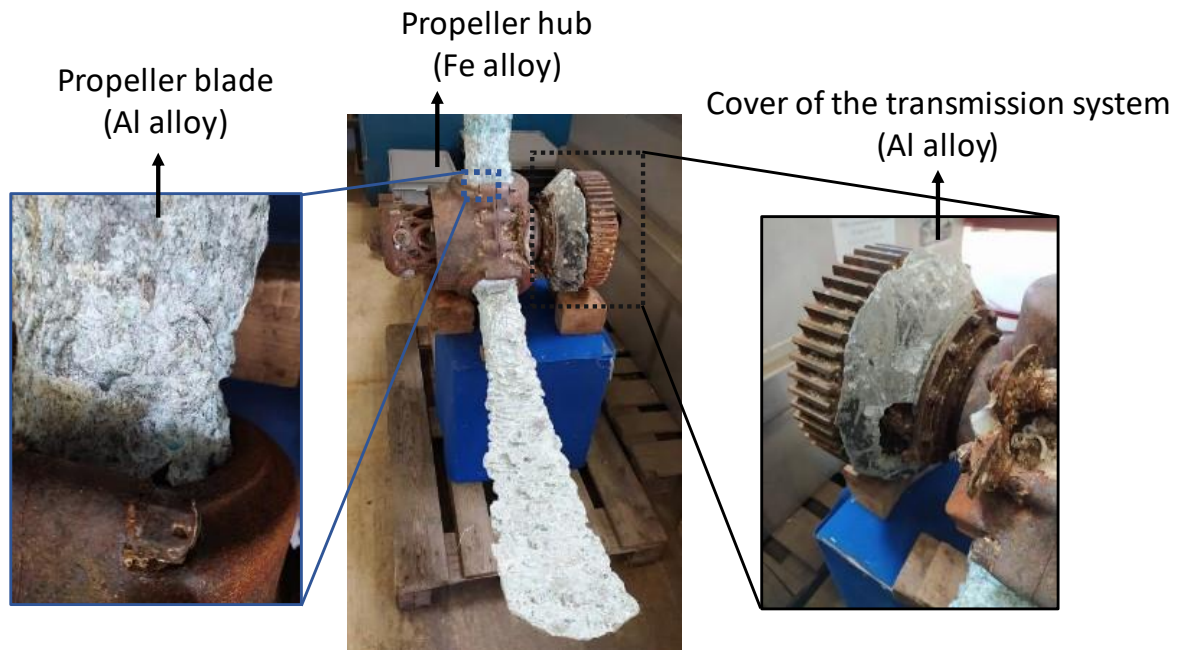
The corrosion behaviour of modern alloys for aircraft applications is extensively studied. However, these analyses are insufficiently performed over real and complex cultural heritage objects, many of which exposed to outdoor conditions and aggressive environments [1]. Besides, characterization of the long-term behaviour of materials exposed to complex environmental conditions is of great challenge. It is known that pure aluminium in outdoor conditions corrodes weakly because it formed spontaneously a protective oxide layer [2]. Unfortunately, aluminium alloys used in WWII planes, especially those from the 2000 series (Al-Cu) known as Duralumin, do not have the same corrosion resistance [3], and different studies have shown several corrosion forms, such as intergranular, exfoliation, pitting, and galvanic corrosion [4]. The galvanic corrosion process is driven by the electrode potential difference between two dissimilar metals and each of the metals acts as either the anode or the cathode [5]. Generally, when the galvanic coupling between Al and Fe alloys is established, the dissolution of Al alloys is accelerated [6].

One of the main challenges in the field of cultural heritage conservation is to be able to determine the stability of the objects against corrosion, requiring techniques that are reliable, fast, and reasonably easy to use. For example, as the cathodic reaction of the corrosion process involves the reduction of dioxygen in presence of surface water, placing the object in an airtight recipient and measuring its oxygen concentration over time could be an interesting alternative, assuming that a faster oxygen consumption indicates a higher corrosion rate [7]. Furthermore, this concept could be extrapolated for analysing the galvanic coupling effect and how the cathode/anode area ratio affects the corrosion rate.

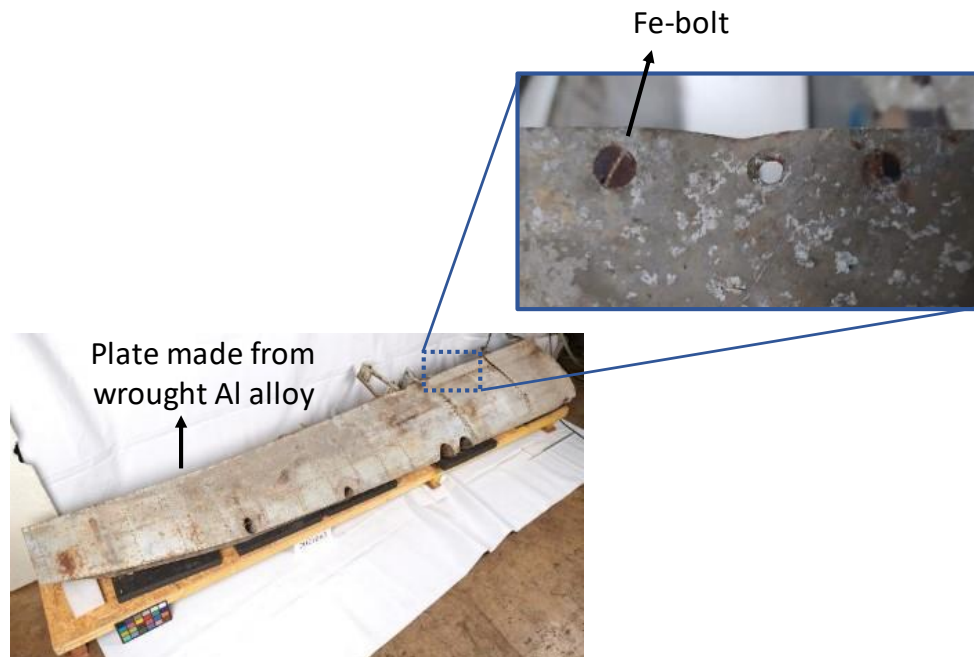
In this context, this work aims to analyze the degradation of two aircraft wrecks from WWII exposed to marine environments for more than half a century and the importance of galvanic corrosion on their level of degradation.

## **Materials and methods**

This study presents the corrosion state of two aircraft wrecks from WWII. These objects were discovered occasionally and recovered from French coasts. The first object is a propeller, probably of a DH Mosquito aeroplane (Fig. 1). This object was found by a trawler in the Fécamp channel (French city seaside to the English Channel) in April 2016. The second one is a Supermarine Spitfire wing discovered three miles from the Plérin coast (Near Saint-Brieuc, also a French city seaside to the English Channel) by a fisherman in 1988 (Fig. 2). After that, this wing was stored in a garden, for about 30 years in an uncontrollable and outdoor environment. For the elemental composition, small-size samples were cut from the objects, then they were embedded in epoxy resin, mechanically grounded up to 4000 SiC paper grade and eventually polished on cloths with diamond paste from 3  $\mu\text{m}$  down to 1  $\mu\text{m}$ . Scanning electron microscopy (SEM) JEOL JSM 5800LV, operated at 20 kV and coupled with Energy Dispersive X-Ray Spectroscopy (EDS), was used to analyse the elemental composition. EDS acquisition was performed on six areas of 500x500  $\mu\text{m}^2$  with a minimum of 100000 counts on each spectrum.



**Fig. 1** Aircraft propeller (blade length 130 cm and maximum chord 26 cm) found in Fécamp (French city seaside to the English Channel), indicating the degradation state of the different components. The Fe/Al area ratio in this object is among 0.4-1, according to the Al piece evaluated.



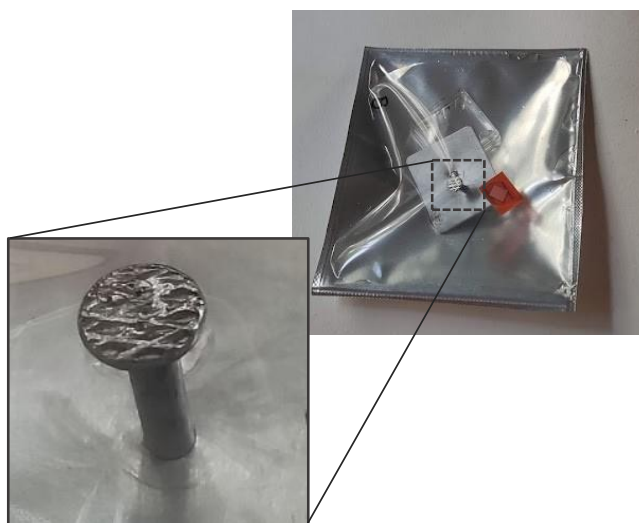
**Fig. 2** Wreck of a Supermarine Spitfire wing (length 436 cm and maximum chord 67 cm) discovered in 1988 near the Plérin coast (French city seaside to the English Channel). The zooming area shows the bolt's degradation and the Al surrounding area. The Fe/Al area ratio between the Fe-bolt and the Al plate is close to 0.1.

To evaluate the galvanic coupling effect and how the cathode/anode area ratio affects the stability of the objects, six different Fe/Al area ratios were selected, increasing the Fe area (0.01, 0.1, 0.2, 0.5, 1 and 10). Iron nails were hammered and fastened to Al plates in pre-made holes of 1.8 mm diameter (Fig3). The samples were enclosed in a transparent bag of Escal<sup>TM</sup> film

with an optical oxygen sensor (PreSens<sup>TM</sup>) steaked at the upper inner part of the bag (seen as a small pink square in Fig. 3).

The oxygen content inside the containers was measured through a fiber optic oxygen meter, Fibox 4. Inside the pockets, the atmosphere was controlled using 1 mL of water/glycerol mixture (for pouches up to 1000 cm<sup>3</sup>), maintaining a relative humidity of 90% [8].

Escal is a durable oxygen barrier film without oxygen consumption tested for at least a year [9]. Moreover, the flexibility of this bag allows us to place samples inside, with different shapes and sizes, reducing the volume around the samples, which makes it advantageous when low oxygen consumption rates are measured [9]. Finally, nine conditions were evaluated, the six Fe/Al area ratio of AW2017-T4 aluminium alloy (similar composition as Hiduminium family) plates coupled with low carbon steel nails, the AW2017-T4 aluminium plate and the low carbon steel nail separately and the control condition without metal (Escal bag with 1 mL of glycerol solution and sensor).



**Fig. 3** Escal bag containing the sample with the Fe/Al area ratio 0.1, a plastic container with 1.0 mL of water/glycerol mixture, 70/30%. The optical oxygen sensor was attached to the upper inner part of the bag using adhesive tape with a central hole of 4mm Ø, allowing oxygen diffusion to the sensor.

A portable Bruker tracer III-SD X-ray fluorescence (XRF) instrument was employed to analyse the surface composition of objects. This equipment is incorporated with a Silicon Drift Detectors (SDD), which provide high-speed data acquisition and light element sensitivity. The spectra were acquired through a 4x3 mm window and a vacuum system that improved the detection of light elements. The duration of each analysis was 120 seconds with voltage and current of 40kV and 13µA, respectively.

## **Results and discussion**

In the first step, analysis by SEM-EDS on polished samples provided information on the corrosion features and the bulk composition of the different metallic alloys. The elemental analysis summarised in Table 1 helped us to identify the alloys used to manufacture the different pieces and objects. The propeller blades and the plate of the wing belong to the Duralumin family, containing aluminium as the base, copper (3.5–4.8 wt.%), magnesium (0.4–1.8 wt.%), and manganese (0.4–1.5 wt.%).

According to the archival studies, several families of aluminium alloys were employed in the United Kingdom for aircraft manufacturing during WWII. The Hiduminium DU Brand characterised by its low magnesium content (below or equal to 1 wt.%) and the Hiduminium 72 with a higher magnesium content (0.8–1.8 wt.%). In this way, Hiduminium DU Brand was probably used to manufacture the propeller blades and Hiduminium 72 for the Al plates of the Supermarine Spitfire wing. [10].

On the other hand, the Al cover was probably made of cast alloy with a composition quite close to the Hiduminium alloy R.R. 50, described as a general-purpose casting alloy regularly employed for cylinder blocks, crankcases and all parts in automobile and aircraft manufacture [11]. The differences that could make us doubt are the silicon and nickel levels slightly lower and higher than the standards, respectively. However, it should be remembered that these alloys date from a war period when exhaustive quality controls of raw materials were not a priority. The hub of the propeller hub and the bolts of the Spitfire wing were identified as ferrous alloys with low traces of manganese and chromium.

**Table 1.** Elemental composition (wt%) by SEM-EDS of the blade and the fuselage plate from the Fécamp propeller and the Spit Fire wing, respectively.

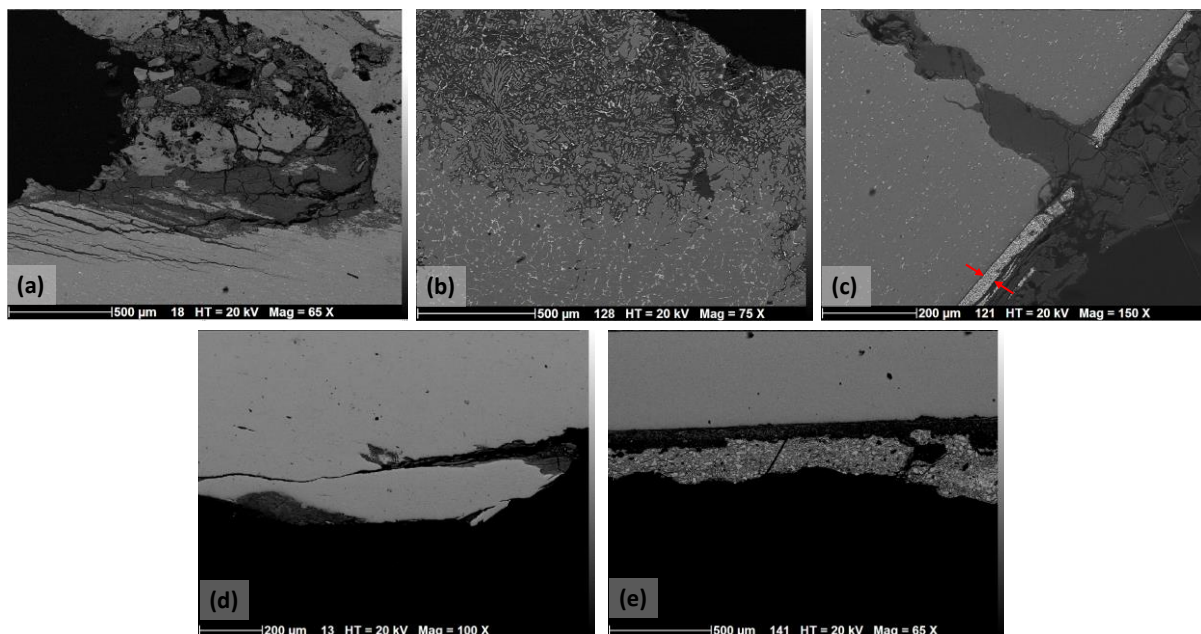
Object	Al	Mg	Si	Mn	Fe	Ni	Cu	Cr
<b>Propeller blades</b>	91.93	0.47	1.26	0.62	0.29	0.04	4.85	
<b>Cover - transmission system</b>	91.06	0.61	3.78	0.02	0.93	0.87	1.61	
<b>Plate-Spitfire wing</b>	94.34	1.20	0.90	0.55	0.33	0.02	4.04	
<b>Propeller hub</b>	-	0.14	0.22	0.88	99.76	-	-	0.89
<b>Bolt-Spitfire wing</b>	-	0.09	0.26	0.62	96.74	1.16	-	0.55

As shown in Fig. 1. the propeller blades are in an advanced state of corrosion. covered by white and blue-green corrosion products. They are known to be hydrated variants of aluminium or copper-aluminium oxides and hydroxides [4]. In addition, intergranular and exfoliation (lamellar) corrosion features are observed in Fig 4a. These types of corrosion are usually exhibited in archaeological elements made from aluminium alloys containing between 3.5 and 5.5% Cu. which is generally recognised as a harmful constituent of these alloys from a corrosion standpoint [12].

In Fig. 2. the aluminium part covering the transmission system of the propeller also exhibits an important degree of deterioration. Fig. 4b shows characteristics of intergranular corrosion on this piece favoured by the presence of nobler AlFeMnSi and Cu-rich phases, making this region more reactive than the bulk of the grains, causing this zone to corrode preferentially, and creating micro galvanic corrosion cells between the cathodic phases and the anodic aluminium matrix [13].

Contrary to the deterioration state of the aluminium parts from the propeller, where it was almost impossible to find evidence of the original protective paint film, the Spitfire wing shows a better conservation state, even after a long exposure time to the marine environment (Fig. 2). On the aluminium plate were observed regions with the remains of the protective paint, approximately 20 µm thick, measured through SEM (Fig 4c). Moreover, evidence of localised pitting corrosion was observed in the regions where the paint protection was broken.

The ferrous pieces from the propeller hub and transmission system showed good homogeneity and uniform corrosion. In contrast, the ferrous bolts from the Spitfire wing showed a more degraded state with thicker corrosion products, as observed in Fig 4e. As shown in Fig. 2, some bolts disappeared, which is attributed to the corrosive process.



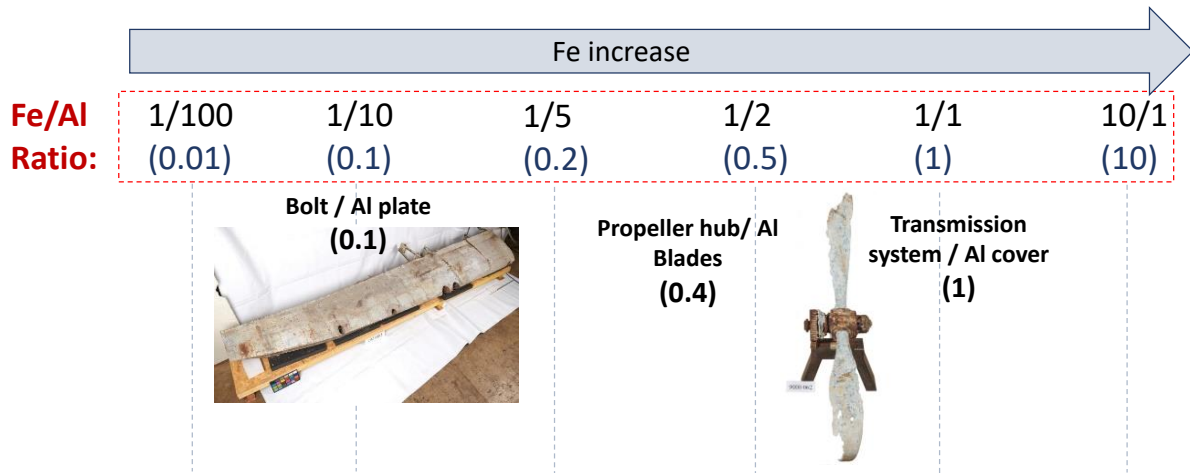
**Fig. 4** Cross-section images from the different parts of the artefacts: (a) Propeller blade of Al, (b) Al cover of the transmission system, (c) Al plate from the Spitfire wing, (d) Propeller hub of Fe and (e) Fe bolt from the Spitfire wing.

The exfoliation, intergranular and pitting corrosion forms observed on the different parts of Al alloys can be explained by the aggressive marine environment as the composition and microstructure of the alloy and the aggressive environmental conditions to which they were exposed during the time they were buried.

XRF analysis revealed the surface composition of the different objects, showing traces of sulphur and chlorine compounds. This information is crucial because the presence of sulphate ions in a marine environment with chloride ions increases the rate of pitting on Al alloys. This situation can be even more detrimental since some studies have shown that alloys such as 2024-T4 and 2014-T3 underwent more severe exfoliation corrosion processes when they were in contact with steel parts, developing a galvanic corrosion process [14,15].

Generally, when the galvanic coupling between Fe alloys and Al is established, the dissolution of Al is accelerated, and the rate of this acceleration is controlled in part by the cathode/anode area ratio. The higher this ratio is, the higher the corrosion rate will be, which could be one of the reasons why the Al parts of the propeller suffered more aggressive corrosion due to their galvanic coupling with the big ferrous part (Propeller hub and transmission system).

The Fe/Al area ratio was determined geometrically and plotted in Fig. 5, showing the ratio difference between the two objects. In the Spitfire wing, the Al proportion is more significant than the Fe one (Fe/Al areas <1). However, this situation is different in the propeller, and the Fe area is larger than that of Al (Fe/Al areas >1). For this reason, to know how much these area ratios affected the corrosion rate of these objects, the six different Fe/Al area ratios of modern alloys were chosen as indicated in Fig. 5 and their oxygen consumption was analysed.

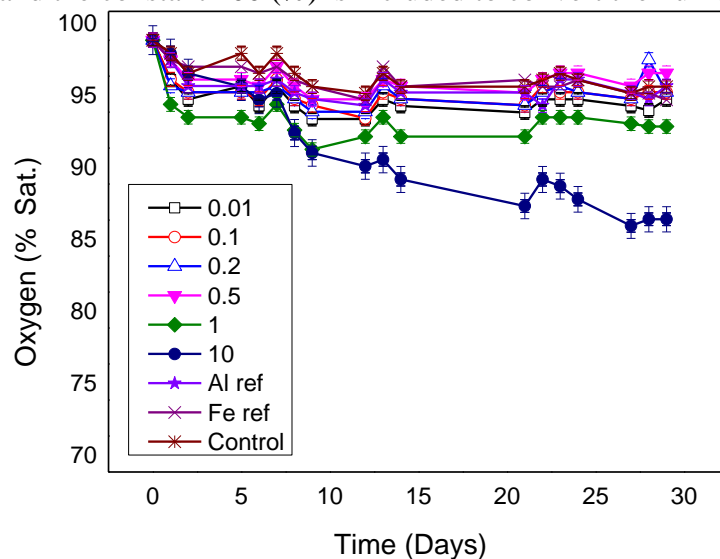


**Fig. 5** The six Fe/Al area ratio used for the oxygen consumption analysis and the relative position of the Spitfire wing and the aircraft propeller.

Fig. 6 shows the measurements of oxygen concentration of the different conditions for 28 days. These curves show a higher oxygen consumption in the first days of analysis; however, their slopes are accentuated after the third day. From them, the oxygen consumption rate was calculated to compare the different samples' results, normalizing the size effect of the parts and the Escal bags. Thus, the oxygen consumption rate may be calculated as:

$$\text{Oxygen consumption rate [mg/day]} = \frac{\text{Air}_{\text{int}} \cdot K \cdot dC/dt}{100}$$

Where  $\text{Air}_{\text{int}}$  is the internal air volume inside the bags, quantified by subtracting the bags and sample volume. The bag volume was measured through buoyancy in water. In this study, the external and internal volumes were considered equivalent, and the magnitude of the borders thermally sealed was negligible. The sample volume was calculated by geometry.  $K$  is the oxygen content in atmospheric air ( $0.276 \text{ mg/cm}^3$  at  $23 \text{ }^\circ\text{C}$ ),  $dC/dt$  is the slope of the oxygen curve (%sat/day), and the constant 100 (%) is included to convert the number to mg/day [16].



**Fig. 6** Oxygen concentration versus time of the six Fe/Al area ratio of Al alloy plates coupled with low carbon steel nails), the Al plate, and Fe nails separately and the control condition (Escal bag with 1 mL of glycerol solution). The slope of the different curves cannot be compared directly as the amount of air inside the bags may vary.



Table 2 summarizes the results of the different conditions studied. In it, we can observe that for the 0.5 Fe/Al area ratio, the oxygen consumption is slightly higher than that consumed by the control system. Besides, the Fe/Al ratios of 1 and 10 show the highest oxygen consumption values of all the systems studied. On the other hand, the samples of Al and Fe not galvanically coupled and enclosed separately showed negligible oxygen consumption values under the same atmospheric conditions (90% RH at room temperature).

**Table 2.** Oxygen consumption measurements for the different conditions studied. The value of oxygen consumed by the control system was subtracted from all samples.

Fe/Al ratio	Volume of sample (cm <sup>3</sup> )	Internal air volume (cm <sup>3</sup> )	Oxygen consumption rate (mg/day)
0.01	5.18	22.0	N
0.1	3.36	33.4	N
0.2	3.48	51.0	N
0.5	3.82	51.1	0.020
1	4.35	65.2	0.184
10	9.05	34.2	0.194
Al plate	3.26	13.3	N
Fe nail	2.68	10.8	N
Control	2.63	10.5	0.015

One thing interesting to recall is that the Fe bolts from the Spitfire wing suffered a more advanced degradation than their surrounded Al plate despite the possible cathodic protection provided by their Al galvanic pair.

Our first hypothesis was to consider that a paint protective layer on the Al plates acted as an electrical insulator between the pieces, thus avoiding the galvanic interaction. However, this was dismissed as there is still electrical conductivity between the iron bolts and the Al plate (with a resistance value of around 0.1 ohms (measured after removing the corrosion products on the parts)).

A second hypothesis still open is to consider the effect of the protective paint layer on this Al surface, which could have changed its galvanic potential towards more noble values, decreasing the galvanic protection effect over the Fe bolts, or even changing the role of which part is acting as anode or cathode. Furthermore, the good condition of the Al plates has been associated with the protective effect of its paint layer, even after a long exposure time in seawater [6].

The results obtained from the oxygen consumption tests are an interesting indication of the harmful effect of the Fe/Al galvanic coupling. However, this is a preliminary study, and complementary experiments, including surface characterisation, and electrochemical analysis are being carried out to understand better whether the objects are actively corroding, why? and the galvanic corrosion roll on these and other objects from WWII. Besides, this is the first step for using this oxygen consumption test on real artefacts considering the galvanic corrosion effect.

## **Conclusion**

Two aircraft wrecks from WWII were analysed: an aircraft propeller probably from a DH Mosquito and one wing from the Supermarine Spitfire, both found in the seabed. The propeller blades and the cover of the transmission system were made of Hiduminium DU Brand and Hiduminium alloy R.R. 50, respectively. They showed a remarkable degradation with features related to intergranular, exfoliation and pitting corrosion processes mainly developed

during the time they were immersed in the aggressive marine environment; these pieces were assembled with the Fe hub and transmission system, which had an area comparable to the Al parts (Fe/Al area ratio 0.4-1). On the other hand, the Spitfire wing with a lower Fe/Al area ratio (0.1) shows a better conservation state, even when it was also exposed to a marine environment for more than half a century. Finally, preliminary results from the oxygen test showed that the oxygen consumption rate increases with a Fe/Al area ratio higher than 0.5. Highlighting, that these oxygen consumption results were obtained in atmospheres without sulfate and chloride aggressive ions and were due to the galvanic coupling interaction in high relative humidity (90% RH).

These results gave us new perspectives for future analysis of the galvanic corrosion effect on objects from WWII. Such as using oxygen consumption tests in more aggressive conditions close to the marine environment and utilising complementary electrochemical measures to help us better understand the anode/cathode activity in these objects.

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