CORROSION-INDUCED HYDROGEN EMBRITTLEMENT IN ALUMINUM ALLOY 2024

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ABSTRACT

Corrosion is a major concern to the structural integrity of aging aircraft structures. The effect of corrosion on the damage tolerance ability of advanced aluminum alloys calls for consideration of the problems associated with the combined effect of corrosion and embrittling mechanisms. The present paper focuses on the observed corrosion-induced embrittlement of 2024 alloy and tries to answer the key question on whether the observed embrittlement is attributed to hydrogen uptake and trapping in the material. The experimental procedures involved: (1) accelerated corrosion testing (EXCO), (2) microstructural investigation of the evolution of corrosion damage (3) hydrogen measurements (4) fractographic analysis of tensile specimens.

Corrosion damage in the alloy initiates with pitting and develops to a network of intergranular corrosion leading to exfoliation of material. Hydrogen is produced during the corrosion process and is being trapped in distinct energy states, which correspond to different microstructural sites. These traps are activated and liberate hydrogen at different temperatures. In alloy 2024, four traps T1 to T4 were identified. Trap T1 is considered to be a reversible trap, which liberates hydrogen continuously at low temperatures. Traps T2, T3 and T4 saturate with exposure time and are considered to be irreversible. The hydrogen front advances with the corrosion front, so hydrogen penetrates in the material through the intergranular paths generated by the corrosion process. Then hydrogen diffuses further in the material establishing a hydrogen affected zone beneath the corrosion zone. Removal of the corrosion layer (equal to the depth of attack) leads to complete restoration of yield strength but only partial restoration of ductility. Removal of the corrosion layer and heating above the T4 activation temperature for hydrogen desorption (to activate all traps) leads not only to complete restoration of strength but also to complete restoration of ductility. Fractographic analysis shows the existence of a quasicleavage transition zone between the intergranular corrosion zone and the ductile corrosion-unaffected material. This quasicleavage zone is embrittled by hydrogen diffusion and trapping. These results constitute evidence of hydrogen embrittlement in Al-alloy 2024.

Today's aircraft design and maintenance follow the damage tolerance methodology. The present paper sheds light at the degradation of ductility due to the corrosion-induced hydrogen embrittlement, which reduces the damage tolerance of the structure. These findings are particularly important for the so-called "aged aircraft", which has exceeded or is near the operational lifetime, but it is still operated by the airlines. If it is decided to continue the operation of such aircraft, a re-determination of lifetime based on the locally degraded material properties appears essential.

1 INTRODUCTION

The structural integrity of aging aircraft structures can be affected by corrosion. As the time of an aircraft structure in service increases, there is a growing probability that corrosion will interact with other forms of damage, such as single fatigue cracks or multiple-site damage. The aging aircraft may have accumulated corrosion damage over the service life and its residual strength depends on possible degradation stemming from corrosion-induced embrittling mechanisms. One characteristic example where failure was attributed to multi-site damage (MSD) has been the Aloha Airlines accident in 1988. Damage was attributed to growth and linkage of multiple fatigue cracks, emanating from rivet holes. Recent investigations in the Hellenic Aerospace Industry (HAI) on firefighting planes has also shown considerable corrosion damage around rivet holes.

There are two key questions regarding this issue: (1) Is there a corrosion-induced degradation of ductility, which in turn degrades damage tolerance and the residual strength of aerostructures? And (2) What is the underlying corrosion-induced embrittling mechanism? The answer to the first question has been given by a long series of experiments, conducted at the Univ. of Patras [1-3] involving mechanical testing of precorroded (in EXCO) alloy 2024. It was shown that (i) degradation of ductility and fatigue life increases with corrosion exposure time and (ii) removal of the corrosion layer restores strength but not ductility. These results indicated the operation of a bulk corrosion-induced embrittlement mechanism. The researchers at the Univ. of Patras pointed that hydrogen embrittlement might be the underlying mechanism.

Other researchers have also considered hydrogen as an embrittlement mechanism in Al-alloys. Speidel [4] reviews recent results, mainly for Al-Mg-Zn alloys. Studies by Scamans et al. [5] of Al embrittlement in humid air, point to the major role of hydrogen. In particular, the intergranular crack path and the reversibility of the phenomenon (recovery of ductility after degassing) support a hydrogen, rather than an anodic dissolution, mechanism. Also, Scamans and Tuck [6] measured hydrogen permeability and stress corrosion resistance of the Al-Mg-Zn alloy, as functions of quench rate and aging treatment, and found similar trends. Regarding hydrogen trapping, it has been shown [7, 8] that lattice defects (vacancies, dislocations, grain boundaries) and precipitates provide a variety of trapping sites for diffusing hydrogen.

Hydrogen traps have mechanistically been classified by Pressouyre [9] as reversible and irreversible, depending on the steepness of the energy barrier needed to be overcome by hydrogen to escape from the trap. Thermal desorption has been successfully used to study hydrogen partitioning in pure cast aluminum and in Al-Cu and Al-Mg_2Si alloys [8]. Accelerated corrosion tests were recently used [10] to characterize corrosion and hydrogen absorption in alloy 2024. In [11] hydrogen evolution from the corroded specimen of Al alloy 2024 was systematically measured as a function of temperature. The existence of multiple trapping states was verified and the quantity and evolution pattern of hydrogen was discussed. In the present work hydrogen uptake and trapping is linked to material embrittlement.

2 EXPERIMENTAL

The material used for the present study was alloy 2024-T351 supplied in thicknesses 1.6-3.0mm. Exfoliation corrosion testing was performed according to ASTM specification G34-90 [12]. It included exposure at 25°C, for 24 hours in a solution containing 234g NaCl, 50g KNO_3 and 6,3ml concentrated HNO_3 (70%wt) diluted to 1 L of distilled water. Exposure times in the EXCO solution ranged from 15 min to 96 hours. The early stages of corrosion (up to 4 hours) were studied by AFM, while the later stages by SEM and metallographic sectioning. An in-house thermal desorption – gas chromatography system was employed in order to measure hydrogen being trapped in the alloy during corrosion. A constant heating rate was applied to the corroded alloy and the amount of hydrogen evolved was measured as a function of temperature. Microhardness testing versus temperature simulating the thermal desorption spectrum of hydrogen trapping was performed, and was set in perspective with the thermal desorption history of trapped hydrogen. Hydrogen profiling was performed by hydrogen measurements after successive material removal. Tensile testing of corroded specimens has been reported in [1, 13] and the results are adopted here. Fractography of tensile specimens was performed in order to identify mode of fracture.

3 RESULTS AND DISCUSSION

Corrosion in this alloy starts in the form of pitting. With exposure time pits become deeper and pit clustering takes place. At 2-4 hours a type of pit-to-pit interaction initiates the process of intergranular corrosion. This type of corrosion has two major consequences. The first is the

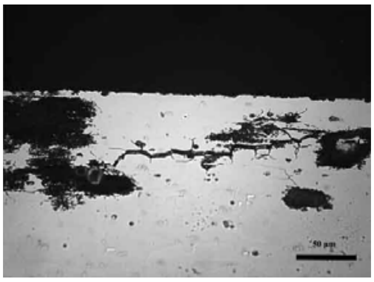

Figure 1: Alloy 2024, 96 hours EXCO exposure, intergranular corrosion leading to exfoliation.

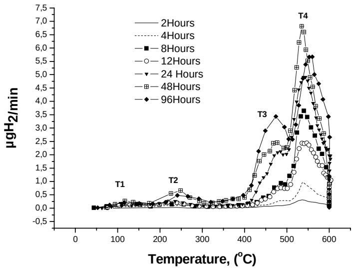

Figure 2: Desorption of H_2 in specimens of aluminium alloy 2024-T3 for continuous heating up to 600 °C.

exfoliation of grains from the surface of the alloy. The second is the opening of paths for the corrosion solution to penetrate in the material interior (FIGURE 1). It appears that this is the way for hydrogen to reach deep in the material. Hydrogen is generated during corrosion. Then it adsorbs on the surface and it diffuses in the alloy, creating a diffusion zone adjacent to the corrosion zone.

It was found that hydrogen is being trapped in distinct energy states, which correspond to different microstructural traps that are being activated at different temperatures (FIGURE 2). The higher the temperature the stronger the trap. In 2024 alloy, four traps T1 to T4 were identified. The quantity of hydrogen liberated from these traps is shown in FIGURE 3. The low temperature trap T1 is the weaker reversible trap and corresponds to hydrogen residing in interstitial sites. Microhardness measurements, performed after subjecting the material to the same thermal cycle used for the hydrogen measurements showed that the corroded material becomes softer. This behaviour is in accordance with theories of hydrogen-induced softening stemming from interaction of hydrogen and dislocations [14] (FIGURE 4). Evolution of hydrogen from the high temperature trap T4 coincides with dissolution of the strengthening phase, as confirmed by computational thermodynamic calculations. This indicates that T4 hydrogen might be trapped in the strengthening phase.

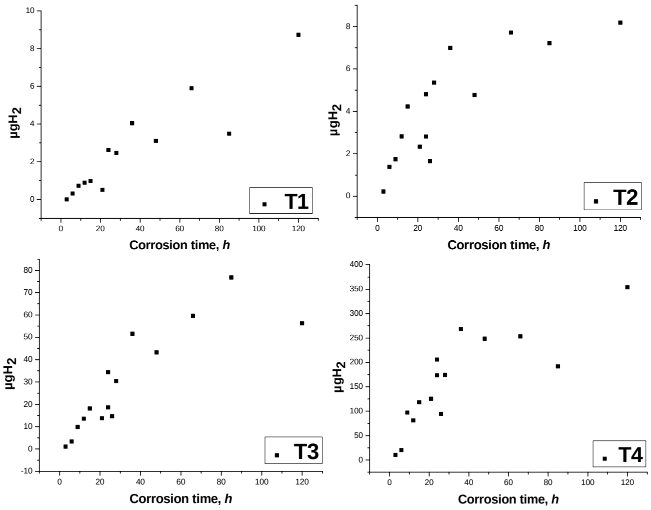

Figure 3: Amount of hydrogen desorpted from the four trapping states (T1-T4) as a function of corrosion exposure time.

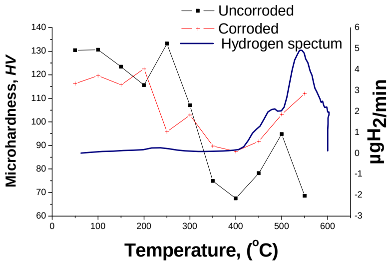

Figure 4: Microhardness profile versus temperature for alloy 2024.

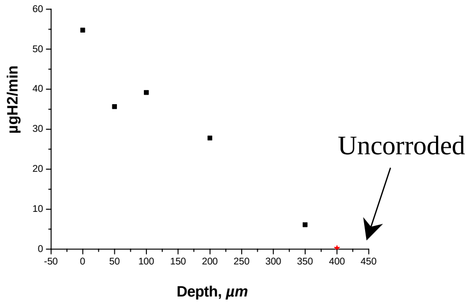

Figure 5: Total amount of H_2 (μg) as a function of depth after 24h of exposure to EXCO solution.

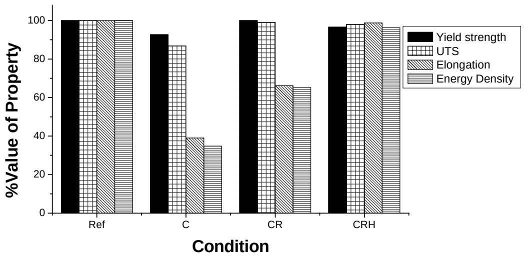

Fig.6: The results of mechanical testing represented as percentages of the respective reference values [13].

Another key question answered by these experiments was how deep in the material is hydrogen introduced. Sequential sectioning provided the hydrogen profile and showed that the hydrogen zone extends below the corrosion zone (FIGURE 5). This means that since hydrogen is generated during corrosion, it reaches to the same depth as corrosion plus a further depth due to diffusion.

In order to link corrosion and hydrogen trapping to strength and ductility, results from tensile testing of corroded samples [13] and corresponding fractographic analysis were undertaken. Tensile test results are shown in FIGURE 6. Corroded material (Condition C) (24h EXCO) has a yield strength 92% and an elongation 39% that of the uncorroded material (Condition Ref). Removal of the corrosion layer restores the yield strength to 100%, while ductility is only partially restored to 66% that of the reference value (Condition CR). This means that an embrittling mechanism still remains in the material even after all surface damage due to corrosion has been removed. Removal of the corrosion layer followed by heating at 495^{o}C restores both the yield strength and elongation to almost 99% of the reference value (Condition CRH). The complete restoration of ductility is attributed to hydrogen desorption by the activation of all hydrogen traps in the alloy. It should be mentioned that the reference values correspond to uncorroded specimens heated and /or ground, in order to correspond to CR and CRH conditions.

The 24 hours EXCO corrosion creates damage which penetrates in a nonuniform way from the surface to the interior of the material, resulting in a depth of attack of 350μm. Below the corrosion layer, a hydrogen zone is established due to the duffusion of hydrogen released by the corrosion reactions. Removal of, a uniform layer equal to the depth of attack, removes all the corrosion damage and all hydrogen trapped in the 350μm surface layer in the alloy. The result is an elongation increase to 66% of the reference value. However, part of the hydrogen zone still remains. The heating of the alloy to 495°C (at the T4 state) removes all hydrogen from that zone by desorption and restores all ductility back to the original value. Fractography of the tensile samples (FIGURE 7) showed that below the intergranular fracture zone at the surface, which is

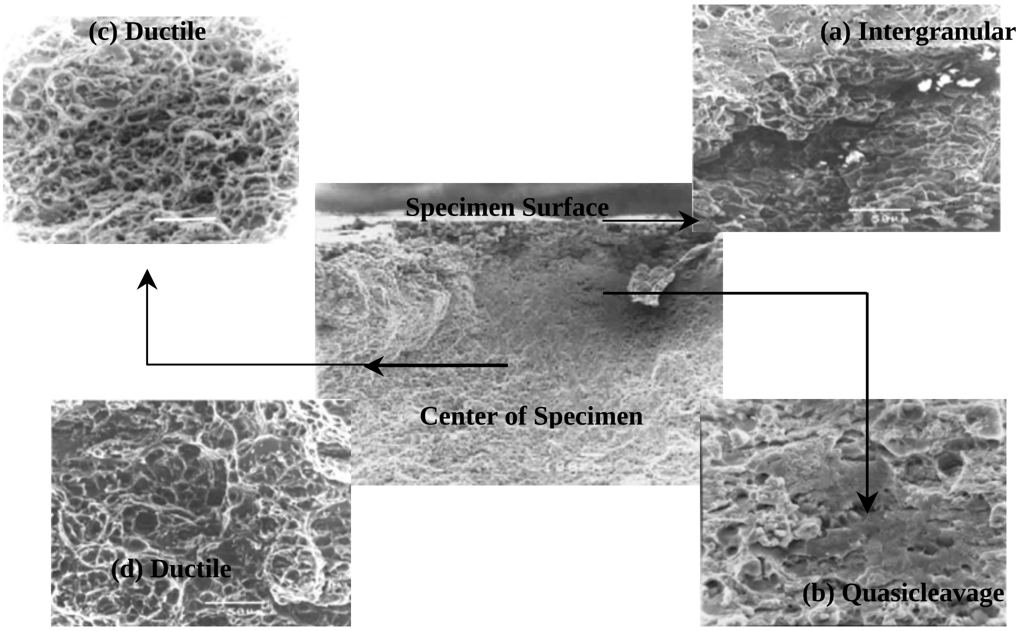

Figure 7: Fracture surfaces of condition C (corroded 24h) specimen. Individual photos correspond to different modes of fracture from the specimen surface through the centre of the specimen.

due to corrosion, there is a quasicleavage transition zone before the fracture mode turns to the ordinary dimple ductile fracture of the unaffected material. This quasicleavage zone has been embrittled by hydrogen diffusion and trapping. Removal of that hydrogen by heating restores all ductility. These results provide evidence of hydrogen embrittlement in 2024 alloy.

4 CONCLUSIONS

The experiments performed in this work led to the following conclusions regarding corrosion-induced hydrogen embrittlement in aircraft Al-alloys:

1. Hydrogen is produced during the corrosion process and is being trapped in distinct energy states, which correspond to different microstructural sites.
2. The hydrogen front advances with the corrosion front, through the intergranular paths generated by the corrosion process and hydrogen diffuses further in the material establishing a hydrogen-affected zone beneath the corrosion depth of attack.
3. Removal of the corrosion layer (equal to the depth of attack) leads to complete restoration of yield strength and partial restoration of ductility. Removal of the corrosion layer and heating above the T4 activation range (to activate all traps) leads not only to complete restoration of strength but also to complete restoration of ductility.
4. Detailed fractographic analysis showed the existence of a quasicleavage transition zone between the intergranular corrosion zone and the ductile corrosion-unaffected material. This quasicleavage zone has been embrittled by hydrogen diffusion and trapping.

Removal of hydrogen by heating restores all ductility. These results constitute evidence of hydrogen embrittlement in Al-alloy 2024.

6 ACKNOWLEDGEMENTS

Part of this work has been financially supported by the Greek Secretariat of Research and Technology (GSRT) and by AirBus.

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