CHARACTERIZATION OF TRAPPED HYDROGEN IN
EXFOLIATION CORRODED ALUMINIUM ALLOY 2024

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Introduction

Stress corrosion and corrosion fatigue represent major threats to the structural integrity of aircraft
structures and have been extensively investigated [1–3]. Among others, Pantelakis et al. [4] observed
dramatic degradation of toughness and ductility of Al-Li alloys 2091 and 8090, as well as conventional
2024 alloy in several types of accelerated corrosion tests. Based on a comparison of mechanical
properties (in particular fracture energy density and fracture strain) of naturally and artificially corroded
specimens, they chose the exfoliation accelerated corrosion test to simulate natural corrosion [5].

The above behavior has been attributed by many investigators to hydrogen embrittlement. Hydrogen
-produced during corrosion- has been accused of diffusing to the interior, leading to material embrittle-
ment through hydrogen-metal interactions [6,7,8]. Despite the lack of a universally accepted hydrogen
embrittlement mechanism, a generally recognized common feature is that some critical concentration of
hydrogen must build-up at potential crack sites, for failure to initiate. Thus, the distribution of hydrogen
inside the metal and its pattern of migration are of paramount importance in understanding the
phenomena and designing alloys with improved behavior.

It has been shown [9,10] that lattice defects (vacancies, dislocations, grain boundaries) and precip-
itates provide a variety of trapping sites for diffusing hydrogen. Hydrogen traps have mechanistically
been classified by Presouyre [11] as reversible and irreversible, depending on the steepness of the
energy barrier needed to be overcome by hydrogen to escape from the trap. For example, during a
degassing experiment reversible traps will release hydrogen continuously, while irreversible ones will
do so only after a critical temperature has been reached. This is the temperature at which the probability
of a single jump out of the steep trap becomes nonnegligible.

Reversible and irreversible traps may play different roles during an actual experiment [12]. In
particular, irreversible traps will always act as sinks for hydrogen, whereas reversible traps may act as
sinks or sources depending on initial hydrogen charging of the lattice. A uniform distribution of
irreversible traps is believed to provide a beneficial effect in alloy behavior under embrittling
conditions, by arresting diffusing hydrogen and thus delaying its build-up at the crack sites [13].
When crack nucleation and growth is along the grain boundaries, boundary chemistry may be playing an important role. Various studies on Al-Mg-Zn alloys [14,15,16] have indicated that alloying elements (and in particular Mg) are segregated on the grain boundary. Tuck [17] proposed that Mg hydride forms at grain boundaries and is responsible for material embrittlement. In an effort to explain the connection between Mg-H interaction and material embrittlement, Song et al. [18] recently showed that stress corrosion and fatigue crack growth rates increase with the concentration of solid solution Mg on grain boundaries. The same authors theoretically calculated a decrease in the intergranular fracture work with both Mg and H segregation.

Useful insight in the nature and intensity of hydrogen traps can be offered by studying the temperature needed to break these bonds. Thus, thermal analysis techniques have been used for a variety of alloys [17], [19]. In particular, thermal desorption has been successfully used to study hydrogen partitioning in pure cast aluminum [20] and in Al-Cu and Al-Mg,Si alloys [9], and hydrogen diffusion in Al-Li alloys [21]. Among other findings, these studies show that, for aluminum alloys, the heat of chemisorption is lower than the activation energy for lattice diffusion of hydrogen. Thus, the layer of passive oxide -formed on the surface of aluminum alloys- does not mask the bulk trapping states and the results of thermal analysis are meaningful.

Accelerated corrosion tests were recently used by Hassiotis et al. [22] to characterize corrosion and hydrogen absorption in the less studied but widely used Al-Cu alloy 2024. In the present work, hydrogen evolution from corroded specimen of Al alloy 2024 is systematically measured as a function of temperature. The exfoliation test [23] is used as a representative accelerated corrosion method and different exposure times are tested. The existence of multiple trapping states is verified and the quantity and evolution pattern of hydrogen is discussed.

**Material and Experimental Procedure**

The material tested is 1.8 mm thick 2024 T3 aluminum alloy plate for aerospace constructions. The chemical composition is the following (wt%): 0.50Si, 0.50Fe, 4.35Cu, 1.5Mg, 0.10Cr, 0.25Zn and 0.15Ti. Strips of this plate, 2.5 mm wide and 40 mm long, are cut at right angles to the rolling direction and are used in the exfoliation test. The large surface-to-volume ratio of the specimen is chosen with a view to decreasing the hydrogen evolution time and increasing the sensitivity of the measurements.

The exfoliation accelerated corrosion test is described in ASTM specification G34–90. Preparation of the corrosive solution involves mixing 234 g NaCl, 50 g KNO₃ and 6.3 ml concentrated HNO₃ (70% wt) and diluting to 1 L with distilled water. The quantity of solution used is proportional to the specimen external surface area, with a minimum amount of 10 ml per cm² of specimen surface.

Exposure takes place in a thermostatic air-bath, with the temperature kept constant at 22±0.5°C. Tight temperature control was deemed necessary, as the first experiments at room conditions showed considerable scatter in the quantity of hydrogen measured, which was attributed to a 3–4°C daily temperature variation. The effect of temperature was verified by conducting representative tests at 20°C, which led to a 20–30% decrease in the quantity of hydrogen measured.

Experiments are conducted with specimen exposed to the corrosive solution from 3 up to 120 hours. Specimen cleaning, after removal from the corrosive solution, involves soaking in concentrated HNO₃, rinsing in distilled water and thoroughly drying in warm air. The entire cleaning process lasts 2–3 minutes and the hydrogen evolution pattern (subsequently described) indicates that hydrogen loss during this period of time is insignificant.

Hydrogen evolves with controlled heating in an inert atmosphere and is measured by a gas chromatograph. The specimen is placed in a 10 mm diameter quartz tube and is held in place by an inert porous bottom (quartz wool). The tube is inserted in a temperature controlled (±1°C), vertical furnace
and is heated at a controlled rate. High-purity nitrogen continuously flows through the tube at a rate of 20 ml/min, and is then driven to a gas chromatograph equipped with a TCD detector. Calibration runs were performed using standard H₂-N₂ samples. Blind experiments were conducted with an empty tube heated to 600°C and no hydrogen was detected.

The rate of heating is an important parameter in the experiments. A very slow rate (typically 0.5°C/min), followed by extended constant-temperature ramps, was used initially to accurately detect the temperatures at which hydrogen first appears. This procedure is adopted to avoid overlap of desorption fields from different trapping states. However, quantitative estimate of total amount evolved at each stage is awkward with this setup; small quantities of hydrogen evolve for extended periods of time and the integration of the concentration versus time curve is not reliable. Thus, after detection of the temperatures at which hydrogen first appears, the bulk of the experiments are conducted at an optimum heating rate (5–6°C/min), which permits separation of the peaks and reliable integration.

**Experimental Results and Discussion**

Hydrogen concentration in the purge stream is recorded as a function of time and of specimen temperature inside the furnace. The concentration versus temperature curves for some representative cases are shown in Fig. 1. Different curves correspond to specimens with varying exposure time to the exfoliation solution. Multiple peaks are observed, attributed to different trapping states. Based on the previously mentioned, low heating-rate experiments, the onset of the peaks labeled as T2, T3 and T4 occurs at 200, 410 and 500°C respectively. These represent critical temperatures, below which no hydrogen evolution from the respective states is observed, even if the specimen is exposed to a constant, lower temperature for an extensive time period. According to Pressouyre [11], the existence of a critical temperature classifies states T2, T3 and T4 as irreversible.

Trapping state T1 is found to release hydrogen continuously at lower temperatures. This is demonstrated by prolonged heating of the specimen at 100°C, which results in evolution of the same total amount of hydrogen as calculated by integration of peak T1. Thus, T1 is considered a reversible trap. Additional trapping sites are possible, as indicated by arrows in Fig. 1. In particular, the shoulder before the T3 peak could be the result of overlap of two evolution processes. However, the amount of hydrogen associated with these hypothetical states seems small compared to the hydrogen contained in states labeled T1 to T4.
Total quantity of hydrogen in each trapping state is estimated by integrating the original concentration-versus-time data to calculate the area under each peak. Results for the four peaks are shown in Figures 2 (a, b, c and d), where the amount of hydrogen (expressed in ppmw relative to the specimen weight) is plotted as a function of exposure time in the exfoliation solution.

The three strong traps T2, T3 and T4 share common features. Linear increase of the amount of hydrogen with exposure time is initially observed, followed by asymptotic approach to a constant value. This behavior is reminiscent of a saturation process by depletion of available active sites. These peaks appear to have a skewed gaussian shape, which is consistent with a combination of a detrapping and a diffusion process [24].

State T4 reaches a plateau concentration of 1200 ppmw after \( \sim 35 \) h exposure in the exfoliation solution, while states T2 and T3 saturate to concentrations 40 ppmw and 300 ppmw respectively, after the lapse of \( \sim 60 \) h. The fact that hydrogen desorbs from state T4 at the highest temperature of all identified trapping states indicates that T4 is energetically favored. The fact that this is the first state to become saturated further supports the above result.

The amount of hydrogen in the T1 state (Fig. 2a) increases linearly with exposure time, and no saturation is evidenced up to an exposure of 120 hours in the exfoliation solution. Since it is the lowest energy state observed, T1 could in principle be associated with adsorbed hydrogen. However, in aluminum alloys the heat of chemisorption is lower than the migration energy and no peak should appear.

It is interesting to note that preliminary results of mechanical tests, performed for the alloy 2024 by Pantelakis et al. [5], indicate that degradation of mechanical properties with exposure time proceeds rapidly at the beginning and then reaches a minimum plateau, which is approached after a lapse of roughly 40–50 hours. This agreement in time-scales between hydrogen saturation and mechanical degradation argues in favor of a significant role of at least one of the trapping states T2, T3 and T4 in the process of stress corrosion and corrosion fatigue.
The physical origin of the above trapping states is difficult to identify solely from thermal analysis. However, some speculations can be made based on information in the literature. Given the fact that T1 is a low energy state and -when compared to the other states- relatively unsaturable, it would appear that this trapping state is related to hydrogen at interstitial sites. The continuous increase in the amount of hydrogen with exposure time to the exfoliation solution is attributed to the creation, by the corrosion process, of new penetration paths for hydrogen (intergranular cracks and surfaces).

Trapping state T2 is an intermediate energy state which saturates with relatively little hydrogen. A possible physical origin of this trap is the interface between the Mg2Si precipitate and the matrix lattice. The β precipitate is incoherent with the matrix and the interfacial dislocations which exist around it can trap hydrogen. This has been shown by Saitoh et al. [9], using tritium autoradiography.

The critical temperature of 410°C, below which no hydrogen evolves from state T3 compares favorably with the thermal decomposition temperature of MgH2 as reported by Tuck [17] (450°C with a heating rate of 50°C/min which should bias the peak to higher temperature). Thus, trapping state T3 could tentatively be associated with Mg hydride. It has been noted by Saitoh et al. [9] that Mg is bonded to Si by a strong ionic bond which precludes formation of MgH2. However, Mg content in the 2024 alloy presently tested is in roughly 40% excess over the stoichiometric analogy with Si and -if saturated-results in a 500ppmw concentration of hydrogen. This estimate compares favorably with the plateau of 300ppmw shown in Fig. 2c.

Finally, an indication for the origin of state T4 is provided by the equilibrium-phase-fraction versus temperature diagram for alloy 2024 (calculated by the computational alloy thermodynamics software ThermoCalc [25]). The critical temperature of 500°C, which marks hydrogen evolution from state T4, coincides with the dissolution of the Al2Cu precipitate. Thus, trapping state T4 should be associated with this phase. Indeed, it has been demonstrated by tritium autoradiography [9] that the bulk of the θ precipitate can serve as a hydrogen trap.

Long-term goal of this research is the correlation of properties of accelerated corroded specimens with those of naturally corroded ones. This would permit reliable estimation of remaining strength and useful life of structures exposed to natural corrosion, based on simple laboratory tests. The amounts and trapping states of hydrogen contained in a corroded specimen could potentially serve as a criterion for such a correlation.

**Conclusions**

1. Four major hydrogen trapping states have been identified by thermal analysis of exfoliation corroded specimens of aluminium alloy 2024; one is reversible (T1) and the other three (T2, T3, T4) irreversible with critical evolution temperatures of 200, 410 and 500°C respectively.
2. The amount of hydrogen in each state correlates well with exposure time in the exfoliation solution. Hydrogen in state T1 increases linearly with exposure time, whereas hydrogen in states T2, T3 and T4 approaches saturation after exposure of 35–60 h.
3. It is conjectured that state T1 is related to hydrogen at interstitial sites, state T2 originates from the interface between the β precipitate and the matrix, state T3 is associated with hydride formed with the excess Mg and state T4 is related to the θ phase.

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