

UNIVERSITY OF THESSALY
SCHOOL OF ENGINEERING
DEPARTMENT OF MECHANICAL ENGINEERING

**Hydrogen Trapping and Embrittlement in Precipitation Hardening
Al-alloys**

by
Styliani Diamantopoulou

Submitted in partial fulfillment of the requirements for the degree of Diploma
in Mechanical Engineering at the University of Thessaly

Volos, 2023

© 2023 Styliani Diamantopoulou

All rights reserved. The approval of the present D Thesis by the Department of Mechanical Engineering, School of Engineering, University of Thessaly, does not imply acceptance of the views of the author (Law 5343/32 art. 202).

Approved by the Committee on Final Examination:

Advisor Dr. Gregory Haidemenopoulos,
Professor, Department of Mechanical Engineering, University of
Thessaly

Member Dr. Eleni Kamoutsi,
Lab Teaching Staff, Department of Mechanical Engineering,
University of Thessaly

Member Dr. Nikolaos Aravas,
Professor, Department of Mechanical Engineering, University of
Thessaly

Acknowledgements

This project was accomplished in the scope of the partial fulfillment of the requirements for the degree of Diploma in Mechanical Engineering at University of Thessaly.

I would first like to express my sincere appreciation to my supervisor Dr. Gregory Haidemenopoulos, his persistent help throughout this project and his guidance led to the completion of my Diploma Thesis.

Further, I am particularly grateful to Dr. Eleni Kamoutsi and Dr. Nikolaos Aravas for accepting to take part in the three-member evaluation committee of my Diploma Thesis.

I would also like to express my gratitude to my parents, Stavros and Evangelia, for their continuous support throughout the course of my studies.

Hydrogen Trapping and Embrittlement in Precipitation Hardening

Al-alloys

Styliani Diamantopoulou

Department of Mechanical Engineering, University of Thessaly

Supervisor: Dr Gregory Haidemenopoulos

Professor of Physical Metallurgy

Abstract

Precipitation hardening Al alloys are the alloys that gain their strength from precipitation of second-phase particles (precipitates). These precipitates, however, are possible hydrogen trapping sites, in cases that hydrogen (H) enters and diffuses in the material. Nowadays hydrogen economy plays a significant role in industry and as a result, in a variety of situations, Al alloy materials can be present and operate around hydrogen, where Hydrogen Embrittlement (HE) can occur. The present study investigated the role of precipitates in hydrogen trapping and subsequent HE. The decrease of ductility depending on the conditions of the material, the degradation of the alloys' properties in the presence of hydrogen, the hydrogen diffusion behavior and the mechanisms of embrittlement were analyzed, along with the main H trapping sites. Precipitates, vacancies and pores were found to be preferential features of the microstructure that accumulate hydrogen, and since precipitates, among them, are favorable for the material's strength their characteristics were examined. State of coherency, chemistry, size and morphology were explored in order to find situations with better H trapping and embrittlement resistance. Coherency, small or large size of precipitates and needle-like or rod-like particles seem in general to be less prone to hydrogen trapping. In addition, because there are other microstructural features and defects that trap hydrogen and affect its diffusion and since Al alloys are heat treatable and interact with environment, all these were also studied. Research about dislocations, grain boundaries, vacancies, dispersoids, alloying elements, crack tips, heat treatment, strain, deformations,

surface treatment, environmental conditions, corrosion and the correlation between these and precipitates or hydrogen trapping took place. Diffusion of hydrogen through dislocations, formation of precipitates at grain boundaries and decrease of hydrogen diffusivity due to deformation are some representative associations that affect HE. Lastly, the beneficial effects of the precipitates were investigated because precipitates can reduce diffusion rate and trap hydrogen, limiting the matrix hydrogen, for some materials and at a constricted environment. At the end of the study, general conclusions and some guidelines for designing hydrogen tolerant Al alloys were presented.

Key words: precipitation hardening, Al alloys, hydrogen (H), hydrogen trapping, hydrogen embrittlement, second-phases, precipitates, trapping sites, TDS analysis, coherency

Παγίδευση και Ψαθυροποίηση Υδρογόνου σε Θερμοσκληρυνόμενα Κράματα Αλουμινίου

Στυλιανή Διαμαντοπούλου

Τμήμα Μηχανολόγων Μηχανικών, Πανεπιστήμιο Θεσσαλίας, 2023

Επιβλέπων Καθηγητής: Δρ. Γρηγόρης Ν. Χαϊδεμενόπουλος

Καθηγητής Φυσικής Μεταλλουργίας

Περίληψη

Τα θερμοσκληρυνόμενα κράματα αλουμινίου είναι τα κράματα που αποκτούν την αντοχή τους από την καθίζηση ενδομεταλλικών ενώσεων (ιζήματα). Τα ιζήματα αυτά ωστόσο είναι πιθανά σημεία παγίδευσης υδρογόνου, σε περιπτώσεις που το υδρογόνο έρχεται σε επαφή και διαχέεται στο υλικό. Στις μέρες μας η οικονομία του υδρογόνου παίζει ένα σημαντικό ρόλο στην βιομηχανία και έτσι, σε ποικίλες περιπτώσεις, υλικά από κράμα αλουμινίου βρίσκονται και λειτουργούν ανάμεσα σε υδρογόνο, προκαλώντας Ψαθυροποίηση Υδρογόνου. Η παρούσα μελέτη ερεύνησε τον ρόλο των ιζημάτων στην παγίδευση και επακόλουθη ψαθυροποίηση από το υδρογόνο. Η μείωση της ολκιμότητας ανάλογα τις συνθήκες του υλικού, η υποβάθμιση των ιδιοτήτων του κράματος παρουσία υδρογόνου, οι τρόποι διάχυσης του υδρογόνου και οι μηχανισμοί ψαθυροποίησης αναλύθηκαν σε συνδυασμό με τα κύρια σημεία παγίδευσης υδρογόνου. Οι ενδομεταλλικές ενώσεις, οι οπές και οι πόροι προέκυψαν τα προτιμητέα στοιχεία της μικροδομής για συγκέντρωση υδρογόνου, και επειδή τα ιζήματα, μεταξύ αυτών, είναι ευνοϊκά για την αντοχή ενός υλικού τα χαρακτηριστικά τους εξετάστηκαν. Το επίπεδο συνοχής, η χημεία, το μέγεθος και η μορφολογία τους ερευνήθηκαν, ώστε να βρεθούν καταστάσεις με καλύτερη αντίσταση στην παγίδευση και ψαθυροποίηση υδρογόνου. Η ύπαρξη συνοχής, το μικρό ή μεγάλο μέγεθος στα ιζήματα και σωματίδια σε σχήμα βελόνας ή βέργας φάνηκε πως γενικά είναι λιγότερο επιρρεπή στην παγίδευση υδρογόνου. Επιπρόσθετα, καθώς υπάρχουν και άλλα στοιχεία και ατέλειες της μικροδομής που παγιδεύουν υδρογόνο και επηρεάζουν την διάχυση του και επειδή τα κράματα αλουμινίου προέρχονται από θερμική επεξεργασία και αλληλοεπιδρούν με το περιβάλλον τους, όλα αυτά τα στοιχεία επίσης μελετήθηκαν. Έρευνα σχετικά με τις γραμμοαταξίες, τα σύνορα κόκκων, τις οπές, τις διασπορές, τα κραματικά

στοιχεία, τις ρωγμές, την θερμική επεξεργασία, τις παραμορφώσεις, την επιφανειακή επεξεργασία, τις περιβαλλοντικές συνθήκες, την διάβρωση και την συσχέτιση ανάμεσα σε όλα τα παραπάνω με τα ιζήματα ή την παγίδευση υδρογόνου έλαβε μέρος. Η διάχυση υδρογόνου μέσω των γραμμοαταξιών, ο σχηματισμός ιζημάτων στα σύνορα των κόκκων και η μείωση της διαχυτότητας του υδρογόνου λόγω παραμορφώσεων είναι κάποιες αντιπροσωπευτικές συσχετίσεις που επηρεάζουν την ψαθυροποίηση υδρογόνου. Τελικώς, τα ωφέλιμα αποτελέσματα των ιζημάτων ερευνήθηκαν καθώς τα ιζήματα μπορούν να μειώσουν τον ρυθμό διάχυσης και την παγίδευση υδρογόνου, περιορίζοντας το υδρογόνο στο πλέγμα, για συγκεκριμένα υλικά και σε ένα περιορισμένο περιβάλλον. Στο τέλος της παρούσας μελέτης, παρουσιάστηκαν γενικά συμπεράσματα και μερικές κατευθύνσεις για τον σχεδιασμό κραμάτων αλουμινίου με αντοχή στο υδρογόνο.

Λέξεις-κλειδιά: ισχυροποίηση με καθίζηση, κράματα αλουμινίου, υδρογόνο, παγίδευση υδρογόνου, ψαθυροποίηση υδρογόνου, ενδομεταλλικές ενώσεις, ιζήματα, σημεία παγίδευσης, ανάλυση TDS, συνοχή

Contents

Chapter 1. Introduction.....	1
1.1 Motivation	1
1.2 Literature Review.....	2
1.2.1 Precipitation hardening	2
1.2.2 Hydrogen diffusion and trapping.....	2
1.2.3 Sites of H trapping	3
1.3 Thesis Organization.....	3
Chapter 2. How hydrogen trapping affects ductility and causes hydrogen embrittlement	5
Chapter 3. Role of precipitates on hydrogen trapping.....	13
3.1 Coherency.....	13
3.2 Chemistry.....	16
3.3 Size	19
3.4 Morphology	25
Chapter 4. Interaction between precipitates and defects, features, environment or treatment	27
4.1 Dislocations	27
4.2 Grain Boundaries	28
4.3 Vacancies	30
4.4 Dispersoids	31
4.5 Alloying Elements	33
4.6 Crack Tips.....	35
4.7 Heat Treatment	35
4.8 Strain – Deformations	37
4.9 Surface Treatment	39
4.10 Environmental Conditions.....	39
4.11 Corrosion	43
Chapter 5. Beneficial effects of precipitates.....	45
Chapter 6. Conclusions.....	47
References	52

LIST OF FIGURES

Figure 2-1: Ductility decrease for under-ageing area, peak-ageing area and over-ageing area for three different temperatures. a) for 170 °C, b) for 190 °C and c) for 210 °C [36]	6
Figure 2-2: Schematic presentation of HELP mechanism [19]	8
Figure 2-3: Schematic presentation of HEDE mechanism [19]	8
Figure 2-4: Schematic presentation of AIDE mechanism [19]	8
Figure 2-5: Schematic presentation of a TDS experiment [23]	9
Figure 2-6: Peak1, peak2 and peak3 labeled in the diagram show sites of hydrogen release [14]	10
Figure 2-7: T1, T2, T3 and T4 labeled in the diagram show peaks of the curve that are sites of hydrogen release [29]	10
Figure 3-1: Tritium EM autoradiograph: left) θ' precipitates and silver grains, which indicate hydrogen, observed on the edge of only some precipitates and right) θ precipitates and silver grains observed on the precipitate. [37]	14
Figure 3-2: T4 peak labeled in the diagram liberates more hydrogen and at a higher temperature than the labeled T2 peak, so it is a stronger trapping site [29].....	15
Figure 3-3: Schematic explanation of interaction between shearable (coherent) and non-shearable (incoherent) precipitates [52]	16
Figure 3-4: TEM micrographs: $\text{Al}_2\text{Cu}-\theta$ phase and $\text{Mg}_2\text{Si}-\beta$ phase appear along with the main $\text{Al}_2\text{CuMg}-\text{S}$ phase for AA2024 [8]	17
Figure 3-5: EDS element mapping analyses: $\text{Al}_2\text{CuMg}-\text{S}$ phase appear near cracks, tips and interfaces for AA7068 apart from hardening η - MgZn_2 phase [6].....	17
Figure 3-6: HAADF-STEM micrographs: $\text{Mg}_2\text{Si}-\beta$ phase appear along with the main MgZn_2 η - phase for AA7003 [12].....	18
Figure 3-7: Micrographs of a) and b) OA precipitates, c) and d) MA5 precipitates and e) and f) MA3 precipitates. Comparison between the three conditions, gradual reduction of the size from b) to f) [52].....	19
Figure 3-8: HRTEM micrographs: Left) η' intragranular precipitates after 5h and right) η intragranular precipitates after 48h [13]	20
Figure 3-9: TEM micrographs: intergranular precipitates a) before ageing, b) after 5h of ageing, c) after 20h of ageing and d) after 48h of ageing [13]	21

Figure 3-10: TEM micrographs of a) NA, c) PA and e) OA samples and HRTEM micrographs of b) NA, d) PA and f) OA samples [54]	22
Figure 3-11: diagram shows elongation loss (blue columns) for NA, PA and OA conditions [54]	23
Figure 3-12: Data for cracks number density for NA, PA and OA conditions [54]	23
Figure 3-13: TEM micrograph of grain boundary precipitates of AA7A99 [7]	24
Figure 3-14: Tritium EM autoradiographs: left) β' precipitates and right) β precipitates [37]	25
Figure 3-15: HRTEM images: GPI zones, η' precipitates and η precipitates for 7A99 [7].....	26
Figure 3-16: TEM micrographs: left) GP zones of AA7175 and right) η' and η precipitates for AA7175 [53].....	26
Figure 4-1: Diagram showing grain boundaries' trapping power for hydrogen for 7xxx Al alloy [32]	29
Figure 4-2: Tritium EM autoradiographs: a) grain boundaries with precipitates (for Al-1% Mg2Si alloy) have silver grains, that indicate hydrogen, at the interface while b) grain boundaries without precipitates have no silver grains [37]	29
Figure 4-3: H amount at GBPs [5].....	30
Figure 4-4: TEM: Dispersoids (shown with arrows) trapping for grain and sub-grain [9]	32
Figure 4-5: Mn and H related at the interface between matrix and dispersoid (dashed line) [24]	32
Figure 4-6: Fracture morphology of Al alloy left) standard alloy right) alloy with Mn addition [57]	34
Figure 4-7: Hydrogen content at four different trapping sites in regard with corrosion time for AA2024 [33].....	36
Figure 4-8: Curve for ductility decrease on the diagram, the highest decrease inside over- ageing area [36].....	37
Figure 4-9: Diagram shows decrease in H trapped for strains above 0.06 for AA2024 [15] ...	38
Figure 4-10: Trapped H content for precipitates for 4,5% strain conditions and unloading condition for 7xxx Al alloy [32].....	38
Figure 4-11: Diagram shows D amount for to different charging temperatures for 2xxx Al alloy [23]	40
Figure 4-12: Hydrogen release for 7xxx Al alloy left images) dry environment and right images) wet environment. c) and f) enlarged images of the vertical axes from b) and e) [18]	41

Figure 4-13: Hydrogen amount during exposure time at NaCl solution for AA7046 [28]	42
Figure 4-14: Ductility behavior during exposure time to corrosion solution for AA2024 [36]	42
Figure 4-15: Determination of corrosion layer depth for AA2024 [29]	43
Figure 5-1: Binding energies of different precipitate types. η -MgZn ₂ , S-Al ₂ CuMg and θ -Al ₂ Cu precipitates are more important for precipitation hardening [34]	46

Chapter 1. Introduction

1.1 Motivation

Nowadays Al-alloys are widely used in industry because of the light-weight and good properties [1]. These alloys have been key players in a variety of products and structural materials due to high specific strength, good workability, high corrosion resistance and other good mechanical properties of each alloy [2,3,4]. One main category is the precipitation hardening alloys, which have many beneficial mechanical properties such as high strength-to-weight ratio and energy absorption capacity, low density and good fracture and stress corrosion cracking resistance [5,6,7,8,9]. A combination of these properties is important for a sustainable society so 2xxx, 6xxx and 7xxx series Al-alloys are essential materials in aerospace, automotive, transportation, mobile communication, aviation and electricity production industries [5,6,9,10,11,12]. However, in many cases, problems have occurred for in service Al-alloys with defects, due to Hydrogen Embrittlement (HE) [5,10,13,14,15,16,17,18,19].

At the same time, hydrogen is an element that increasingly gaining the attention of people of science and technology as a solution for more clean transportation and energy storage. Hydrogen energy systems and hydrogen fuel tend to become a part of many industries due to environmental crisis and the attempt of “green” energy sustainability [20,21]. In a variety of applications, such as hydrogen storage, the equipment is made of precipitation hardening Al-alloys [21]. Therefore, there is a need to make sure that the interaction between hydrogen (H) and Al-alloys are safe.

Investigating precipitation hardening Al-alloys (2xxx,6xxx,7xxx) revealed that in an array of cases hydrogen trapping is associated with precipitates (inside precipitates or/and at the interface between precipitates and matrix) [2,10,13,14,15,16,19,22,23]. Consequentially, precipitates and the area around them are related to the degradation because of H, the embrittlement and the failure [11,24]. As a result, research in regard with the role of

precipitates of Al-alloys in hydrogen trapping and embrittlement is essential in order to attempt designing of alloys with more resistance to hydrogen embrittlement. Previous studies have noted this necessity down as well [1,25].

1.2 Literature Review

1.2.1 Precipitation hardening

Precipitation hardening is a method of alloy strengthening. This process is a diffusive phase transformation, which happens with nucleation and growth of second phase particles [26]. The applied heat treatment consists of three steps: i) solution treatment, for diffusion of solute atoms, ii) rapidly quench to room temperature, in order to trap the alloying elements and iii) aging, during which trapped elements precipitate [3]. A uniform distribution of fine particles that is formed, block the motion of dislocations, provide resistance to slip and therefore strengthen the material. It is essential to note that during aging (natural and artificial) there are various metastable phases with different characteristics, formed depending on the aging time and temperature. As a result, there is a precipitation sequence for every alloy, including all metastable and equilibrium strengthening second phases, together with the main phase.

1.2.2 Hydrogen diffusion and trapping

Hydrogen economy and demanding environmental conditions force Al-alloys to be in contact with hydrogen. Metallic hydrogen storage containers, engines and constructions with metallic parts that use hydrogen as a fuel or operate in humid environment [11,27,28] and alloys that suffer from corrosion [10,15,29] are prone to H diffusion and trapping. Atomic hydrogen may come from high-pressure hydrogen gas, electrochemical hydrogen charging or cathodic reactions [13,19] and due to its small size and high mobility it is easy to diffuse and be trapped inside a material [1,19,25]. Diffusion happens after H absorption on the metal surface and dissolution in the material, where distribution of the atoms is influenced by hydrogen concentration gradient [19]. Therefore, hydrogen may occur at microstructural sites because the potential well for these trap sites is deeper than for the interstitial lattice, where theoretically atoms are trapped [30]. Interaction between H trapping and diffusion is complex

because H transport is affected by stress gradients and mechanical loading [13]. Microstructure features trap H and hinder its movement while dislocation movement can force H to immigrate [11,19,28]. The important parameters to measure the above processes are H diffusion coefficient, trap density and trap binding energy [31,32].

1.2.3 Sites of H trapping

The sites of hydrogen trapping are: interstitial sites, dislocations, vacancies, blisters, precipitates, solute atoms, low-angle and high-angle grain boundaries, second phase particles and impurities [10,27,28,31]. Hydrogen traps can be divided by reversible and irreversible depending on the hydrogen steepness of the energy barrier the hydrogen must overcome in order to be liberated [15,29]. Because the division is associated with the binding energy [11] it is reasonable that traps are classified as reversible if there is probability of an atom to jump out of a trap [30,33]. Sites classified as reversible are: interstitial sites, vacancies, dislocations, coherent precipitates and low-angle grain boundaries. Sites classified as irreversible are: incoherent precipitates, semi-coherent interfaces and high-angle boundaries [19,28,29,31]. In most of the cases reversible traps lead to a more sensitive to HE material [11,19,31,34]. However, if there is a high density of reversible traps, HE susceptibility may be low [11].

1.3 Thesis Organization

The rest of the diploma thesis is divided into five sections, which are occupied from Chapters 2-6, respectively. In particular,

Chapter 2 analyzes how hydrogen accumulation and trapping affects ductility of an Al alloy and how this trapping causes Hydrogen Embrittlement for precipitation hardening Al-alloys.

Chapter 3 elaborates the role of different characteristics of the precipitates on hydrogen trapping.

Chapter 4 introduces any possible way for microstructural features and treatment or environmental parameters to affect hydrogen trapping at precipitates and Hydrogen Embrittlement susceptibility.

Chapter 5 exhibits the potential beneficial effects of the precipitates regarding Hydrogen Embrittlement resistance.

Final conclusions of the diploma thesis and guidelines for designing of hydrogen tolerant alloys are presented at Chapter 6.

Chapter 2. How hydrogen trapping affects ductility and causes hydrogen embrittlement

Hydrogen trapped inside the Al alloy material destroys it, causing Hydrogen Embrittlement. During H trapping, ductility of the material is generally decreased [29,35], correspondingly to the degradation of many other mechanical properties [6,19,35]. Alexopoulos et al. [36], found relation between ductility reduction and heat treatment, after conducting artificial ageing and exposure to corrosion environment for a AA2024-T3 alloy. Results show that highest ductility decrease happens before ageing, lowest at the peak-ageing and a partially restoration takes place at over-ageing. Also, lower decrease of ductility happens for lower temperatures. Fig. 2-1 shows the alteration for both the different ageing times and the different temperatures. Concurrently, Kamoutsi et al [29], studied restoration of ductility reduction, using tensile tests, fractography, microhardness measurements and thermal desorption on 2024-T351 pre-corroded alloy. After all the above it is proved that removal of the corrosion layer partially restores ductility and only if there is also an additional heating to release all trapped H ductility is fully restored [24,29]. The fact that with corrosion and H diffusion a hydrogen affected zone is established under the corrosion layer and affects fracture is evidence of a bulk mechanism of embrittlement, as HE [29]. Ductility reduction may cause the alloy's failure.

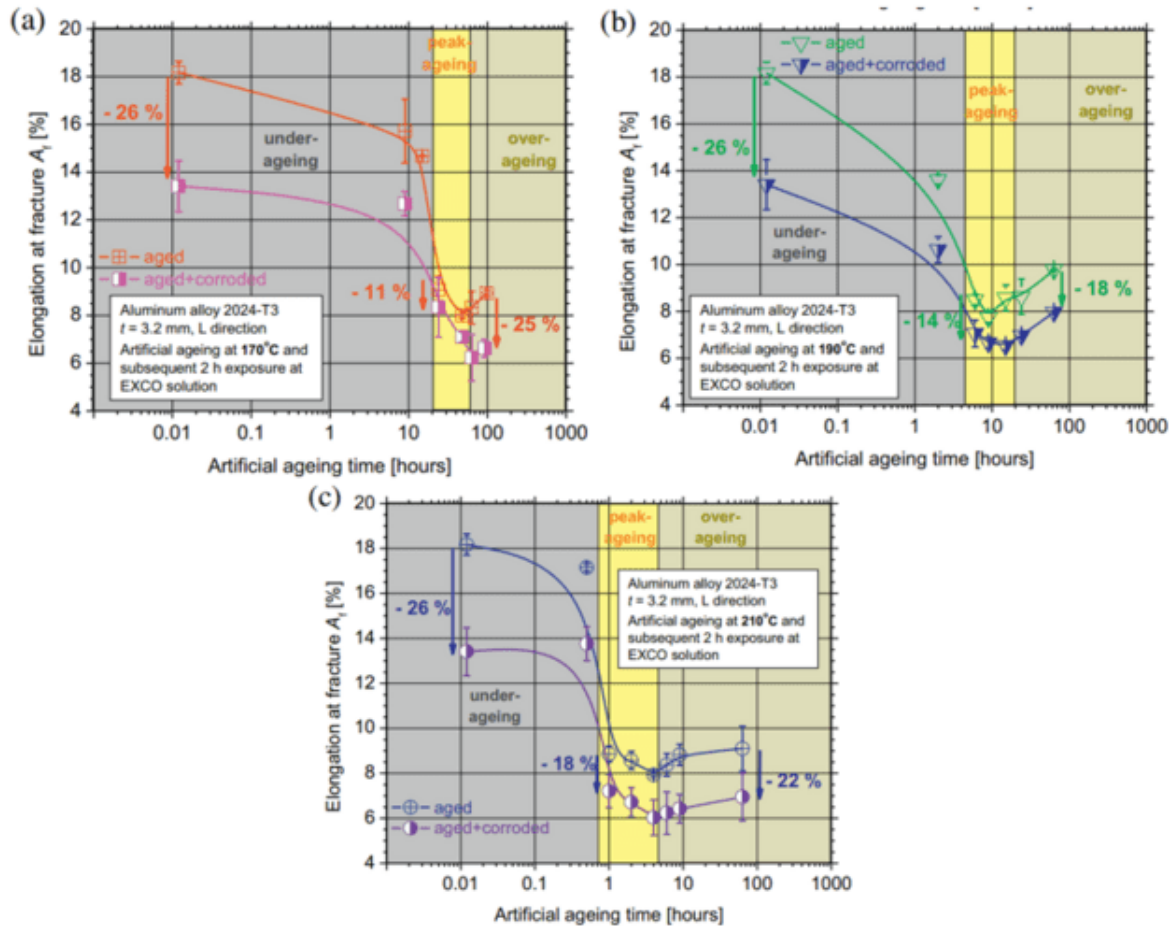


Figure 2-1: Ductility decrease for under-ageing area, peak-ageing area and over-ageing area for three different temperatures. a) for 170 °C, b) for 190 °C and c) for 210 °C [36]

Otherwise, ingress of H in a material degrades mechanical properties and provokes premature failure. Reports state that presence of hydrogen can reduce yield strength [29], local plasticity when accumulated on crack tips [6], tensile strength, fatigue strength and fracture toughness [19]. The reduction of yield strength is associated with corrosion layer on the surface, so removal of this layer completely restores the property [24,29]. Brittle intergranular fracture mode is related to HE in Al-alloys [35], but also quasi-cleavage fracture is maybe connected to HE [36]. An association between these two is described by Kamoutsi et al [29], analyzing that quasi-cleavage zone is a transition between intergranular corrosion zone and ductile H-unaffected material. Precipitates are a potential site for initiation of fracture and a way for propagation of hydrogen-induced quasi-cleavage cracks [32]. Hydrogen absorption and repartitioning in the material is promoted by dislocations and grain boundaries which act as short-circuiting diffusion paths [6,37] and at the same time presence of hydrogen

enhances dislocation mobility [14]. Moreover, crack tips in the material accumulate hydrogen, facilitate dislocation emission [14] and forward crack propagation [6], leading to failure.

All the above cause Hydrogen Embrittlement. In order to quantify HE sensitivity three parameters are proposed. Firstly, Safyari et al [35], calculated “Hydrogen embrittlement susceptibility index (I_{HES})”, using elongations from specimens with and without treatment. In addition, Sun et al [34], defined two parameters to measure the effectiveness of their strategy to mitigate HE. “Improvement of absolute ductility (I_D)” and “Improvement of the H embrittlement index (I_{HEI})”, using ductility measurements before and after strategy is applied.

The mechanism of Hydrogen Embrittlement is not yet fully understood [38], but there are many proposed mechanisms. The most acceptable HE mechanisms are Hydrogen-enhanced Localized Plasticity (HELP), Hydrogen-enhanced Decohesion (HEDE), Adsorption-induced Dislocation Emission (AIDE), Hydrogen-enhanced Strain-induced Vacancy (HESIV), Hydride Formation and Fracture and Hydrogen-induced Phase Transformation (HIPT). HELP mechanism is based on enhancing dislocation movement [38,42], because accumulation of H decreases the resistance of dislocation motion [39,41], causing plastic deformation and promoting macroscopic failure through localized shear [40], as shown in Fig. 2-2. According to HEDE mechanism H inside the material weakens atomic bond due to dilatation of atomic lattice [39] and lowers cohesive strength near a crack tip [41,44] leading to cleavage-like fracture [40], as shown in Fig. 2-3. AIDE mechanism is often considered a combination of both HELP and HEDE mechanisms, as shown in Fig. 2-4, because during this mechanism hydrogen influence the cohesive energy and concurrently facilitate dislocation nucleation on the surface [40]. According to HESIV mechanism, hydrogen reduces vacancy formation energy, forms vacancy-hydrogen clusters, which limit dislocations emission, and provokes an enhanced pinning effect promoting brittle fracture [40,43]. For Hydride Formation and Fracture mechanism there is nucleation and growth of the hydride phase and the subsequent cleavage of the hydride [42], so this mechanism takes place at temperatures that hydride phase is stable and brittle [45]. HIPT mechanism causes phase transformation in presence of hydrogen and stress [41,46], reducing boundary cohesive strength and initiating micro cracks in these regions [46]. HELP, HEDE and HESIV mechanisms can explain reversible HE, while HIPT is mostly connected with irreversible HE [19]. All the above mechanisms are affected by microstructure features like atomic lattice, dislocations, vacancies and crack tips, so the importance of fully understand the interaction between them and hydrogen is revealed after

studying the mechanisms. It is useful to mention that HESIV mechanism is more important in metals with lower vacancy formation energy, like Al [40], because vacancy nucleation is easier.

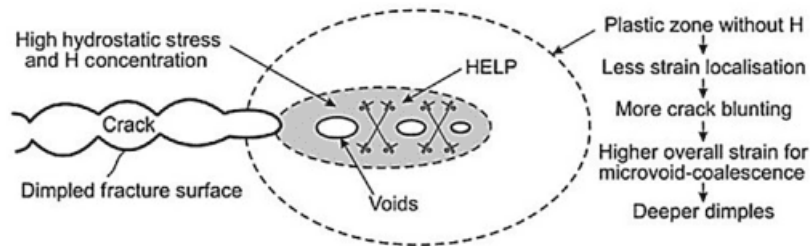


Figure 2-2: Schematic presentation of HELP mechanism [19]

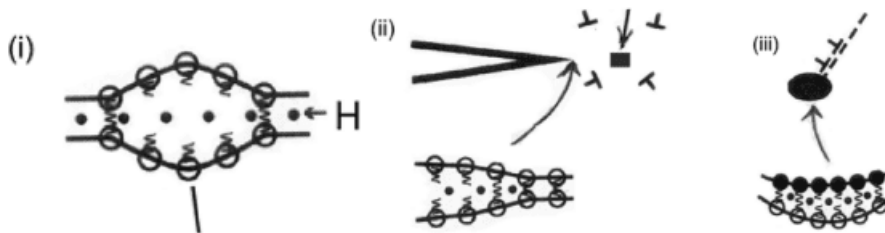


Figure 2-3: Schematic presentation of HEDE mechanism [19]

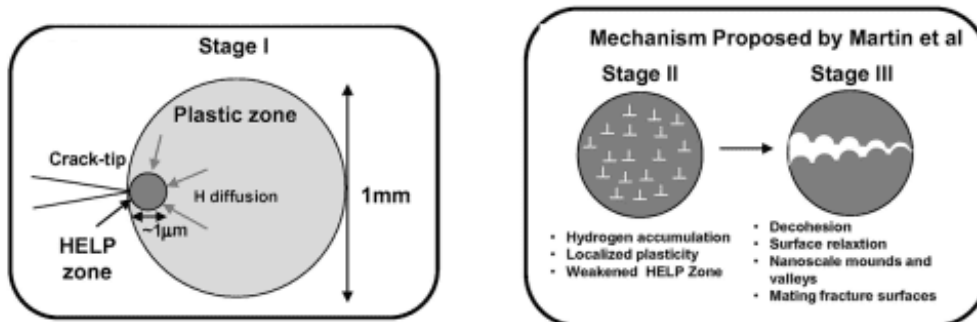


Figure 2-4: Schematic presentation of AIDE mechanism [19]

After noticing H absorption in Al-alloys, researchers grown a need to identify H trapping sites, in order to prevent the trapping or minimize the embrittlement. The most popular and useful approach nowadays is thermal desorption techniques [10,15,23,24,35,47]. In thermal desorption analysis the sample is being charged with hydrogen, or in some cases deuterium D (an isotope of H with a single neutron), and then is subject to an increasing temperature ramp [23]. During the process the sample desorbs hydrogen (or D) from the trap with the lowest to the trap with the highest binding energy between each trap and H. The trap with the highest desorption temperature, which is also the first to saturate, has the highest binding energy and as a result is energetically favored and the strongest trapping site [29].

Thermal Desorption Spectroscopy (TDS) method analyzes the desorption energy of H traps [19]. A TDS system is shown schematically in Fig. 2-5. Curves that introduce the relation between temperature and hydrogen desorption rate are formed after the experiments and they depict peaks at the curves for certain temperatures [10,14,23,29], as shown in Fig. 2-6 and Fig. 2-7. These peaks reveal that when the heating reached the respective temperature there were liberation of hydrogen from a specific trapping site. The desorption energy is estimated based on Kissinger’s method using peak shifts driven by changing the heating rate

and the equation [35,48]:
$$\frac{d(\ln \frac{\Phi}{T_m^2})}{d(\frac{\Phi}{T_m})} = -\frac{E_d}{R}$$
 , where Φ is the heating rate, T_m is the

temperature of the center of the desorption peak, E_d is the desorption energy and R is the universal gas constant. With TDS in combination with hydrogen microprint techniques (HMPT), slow strain rate tensile test (SSRT) [35,48], fractography and observation of stress-strain curves and tables [32] it is feasible to have a good image on H trapping sites and how strong or harmful they may be.

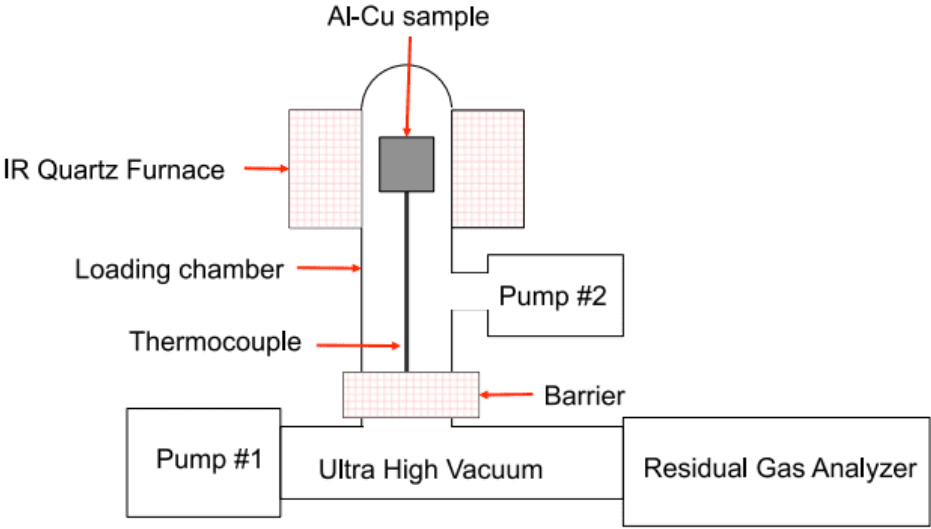


Figure 2-5: Schematic presentation of a TDS experiment [23]

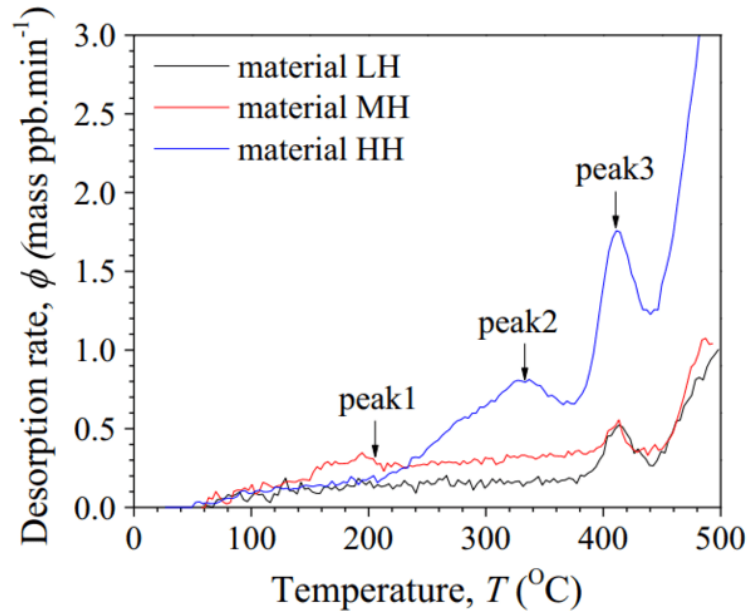


Figure 2-6: Peak1, peak2 and peak3 labeled in the diagram show sites of hydrogen release [14]

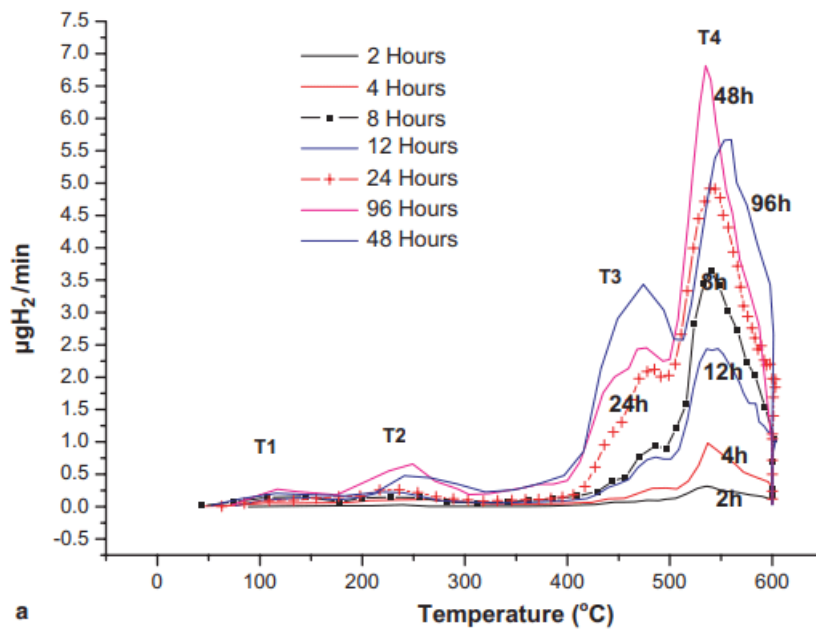


Figure 2-7: T1, T2, T3 and T4 labeled in the diagram show peaks of the curve that are sites of hydrogen release [29]

The first experiments about H trapping were conducted by Young and Scully for pure Al [49] and results showed three peaks. A low-energy trap associated with interstitial sites, a medium-energy trap associated with dislocations and a high-energy trap linked to vacancies. The majority of the findings in regard to trapping sites of H on precipitation hardening Al-alloys are for 2xxx Al-alloys.

So firstly, for 2xxx Al-alloys most of the research conclude four trapping sites, called T1, T2, T3 and T4, from lower to higher energy. In many cases T1 is attributed to interstitial lattice sites, T2 to interfaces between precipitates and matrix, T3 to Mg hydrides and T4 to precipitates of the hardening phase [24,29,33]. In other cases, T3 is linked to dislocations (absence of Mg) [10,15] or T2 originates from stress field between metastable precipitates and matrix [10]. However, the energetically favored T4 trapping sites is still associated with the strengthening phase. Simultaneously, in contrast with the above, one paper shows different information, presenting trapping sites from “weakest” to “strongest” as: interstitial lattice, precipitates, dislocations, GP zones and vacancies [23]. At the same time the authors introduce an opposite opinion on the above findings stating that T1 may be linked to adsorbed hydrogen, T2 linked to lattice, T3 linked to vacancies and T4 linked to Mg.

Secondly, for 6xxx Al-alloys an experiment shows that the trapping site with the highest desorption energy is associated with intermetallic particles [47], so precipitates as well as dispersoids may be connected to the trapping.

Lastly, for 7xxx Al-alloys research based on the binding energy of the trap sites result in six peaks of hydrogen liberation during the heating. The lowest energy peak is associated with dislocations and as the energy is raising peaks originate from grain boundaries, intermetallic particles, vacancies and precipitates, respectively, with the highest binding energy linked to pores [32]. Also, some other experimental works depict dislocations as medium trapping sites, with lowest energy attributed to lattice, and vacancies [35] or grain boundaries [14,48] as energetically favored.

Moreover, it is worth mentioning that older scientific publications had also point out H trapping sites using TEM [37,50]. According to those, for precipitation hardening Al-alloys dislocations, GP zones and interfaces between precipitates and matrix constitute trapping sites.

Analyzing all the above, it is clear that for precipitation hardening Al-alloys high H concentration appears associated with precipitates, vacancies, grain boundaries and pores. However, vacancies, grain boundaries and pores are controversial features that in many cases are not desirable in the microstructure in general. As a result, a thorough investigation of the precipitates, their characteristics, their interfaces, the features that interact with them and the relation between precipitates and the other sites of H concentration has started in many recent publications.

As mentioned above, precipitates come from a heat treatment and end up in their equilibrium phase through a precipitation sequence. For 2xxx series Al-alloys, the precipitation sequence mostly for binary Al-Cu alloys is:

Super Saturated Solid Solution (SSSS) → Cu clustering → Guinier-Preston (GP) zones → θ'' (metastable, coherent) → θ' (metastable, semi-coherent) → θ -Al₂Cu (equilibrium, incoherent) [1,23].

In addition, for 2xxx series, more complex, Al-alloys with more alloy elements than Cu, the precipitation sequence is:

Super Saturated Solid Solution (SSSS) → Guinier-Preston-Bagaryatsky (GPB) zones → GPB₂/S'' (metastable, coherent) → S' (metastable, semi-coherent) → S-Al₂CuMg (equilibrium, incoherent) [8,10,36].

For 6xxx series Al-alloys, the precipitation sequence is:

Super Saturated Solid Solution (SSSS) → Solute Clusters → Guinier-Preston (GP) zones → β'' (metastable, coherent) → β' (metastable, semi-coherent) → β -Mg₂Si (equilibrium, incoherent) [51].

For 7xxx series Al-alloys, the precipitation sequence is:

Super Saturated Solid Solution (SSSS) → Guinier-Preston (GP) zones → η' (metastable, semi-coherent) → η -MgZn₂ (equilibrium, incoherent) [6,12,13,16].

Those are the most common sequences but sometimes there is a different strengthening phase, depending on the composition of the alloy, the ageing and the elastic strain [16]. Also, the phase fraction for each metastable and equilibrium phase depends on the treatment of the alloy [12]. Moreover, for 2xxx Al-alloys β , θ and S precipitates may be created at the same time [8,36] and for 7xxx Al-alloys β precipitates may be created together with η [12]. The concentration of trapped hydrogen changes with ageing time and therefore every investigation on the trapping and embrittlement should contain the effect of all the metastable phases.

Chapter 3. Role of precipitates on hydrogen trapping

The fact that precipitates are a main and energetically favored trapping site for hydrogen inside a precipitation hardening Al-alloy has brought attention of many researchers to study this situation. Many publications mention that some characteristics of the precipitates could affect the interaction between precipitates and hydrogen trapping or embrittlement. The existing research suggests that there is a potential correlation between the behavior of precipitates and chemical composition, ratio of elements, size, shape, hardness, volume fraction, dispersion and interfacial structure [5,14,32,34]. At the same time there are publications that contain some conclusions in regard to a relationship between precipitates coherency, size or morphology, and hydrogen, as analyzed on the next sections. Taking into consideration a great deal of experiments, simulations, results, observations and theories from scientific publications, below there is an analysis of how H trapping may be affected by any of the following characteristics.

3.1 Coherency

The state of coherency is mentioned in many publications as a major parameter of hydrogen and precipitate interaction [10,13,52] and it is generally an important characteristic that distinguishes all metastable and equilibrium phases of a precipitation sequence.

A study for AA 7046 alloys showed that η precipitate would trap more hydrogen than η' precipitate [13] and another study for Al-4% mass Cu showed that θ' is a weak trap site for hydrogen while θ traps H [37], as shown in Fig. 3-1. These findings reveal that incoherent precipitates (η , θ) are more strong trapping sites than semi-coherent (η' , θ'). At the same time, there are mentions for hydrogen trapped in equilibrium, incoherent hardening phases for 2xxx (2024) and 7xxx (7050, 7046) Al alloys [28,36,52]. Partially coherent precipitates can act as barriers for H diffusion and thus these precipitates can be trapping sites, while coherent precipitates limit the quantity of H trapped because they are associated with compression of the lattice [13]. Also, GPB zones and S'' -phase at 2024 alloys have small trapping capacity for hydrogen since they are still coherent with the matrix and H can take interstitial positions in the lattice, so it prefers to do so [36]. Furthermore, for 2xxx all metastable and equilibrium precipitate phases have the ability to trap hydrogen [23], while for 6xxx it is mentioned that GP zones have no trapping power [37]. All the above reveal a higher trapping capacity for

incoherent precipitates, a medium for semi-coherent and a weak trapping for coherent precipitates.

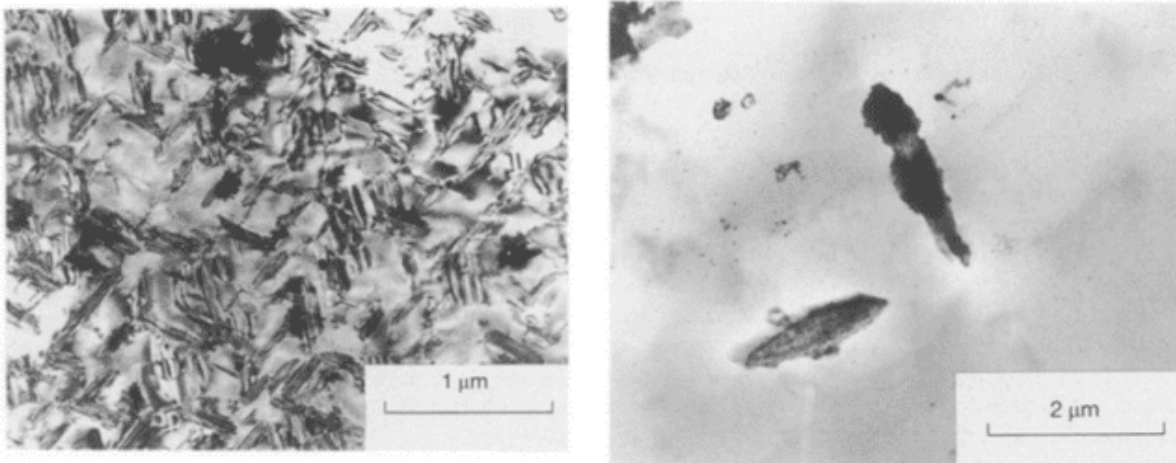


Figure 3-1: Tritium EM autoradiograph: left) θ' precipitates and silver grains, which indicate hydrogen, observed on the edge of only some precipitates and right) θ precipitates and silver grains observed on the precipitate. [37]

The TDS experiments and the studies for the energetically favored trapping sites for H trapping further argue that the loss of coherency may promote H trapping around or inside precipitates. The classification of the trapping sites using “labels” from T1 to T4, leads to trapping site T2 and T4 to be related to precipitates. T2 trapping state is associated with stress field of coherent GP zones or S'' precipitates or the interfaces between the strengthening phases (S and θ) and the matrix (so semi-coherent precipitates) for 2024 Al alloys (T3, T351) while T4 is associated with the S -phase, which is incoherent [10,24,29]. As shown in Fig. 3-2, T4 is a stronger trapping site for hydrogen than T2. As a result, it is, once more, confirmed that the incoherent precipitates are more dangerous trapping sites for Hydrogen Embrittlement than semi-coherent or coherent precipitates.

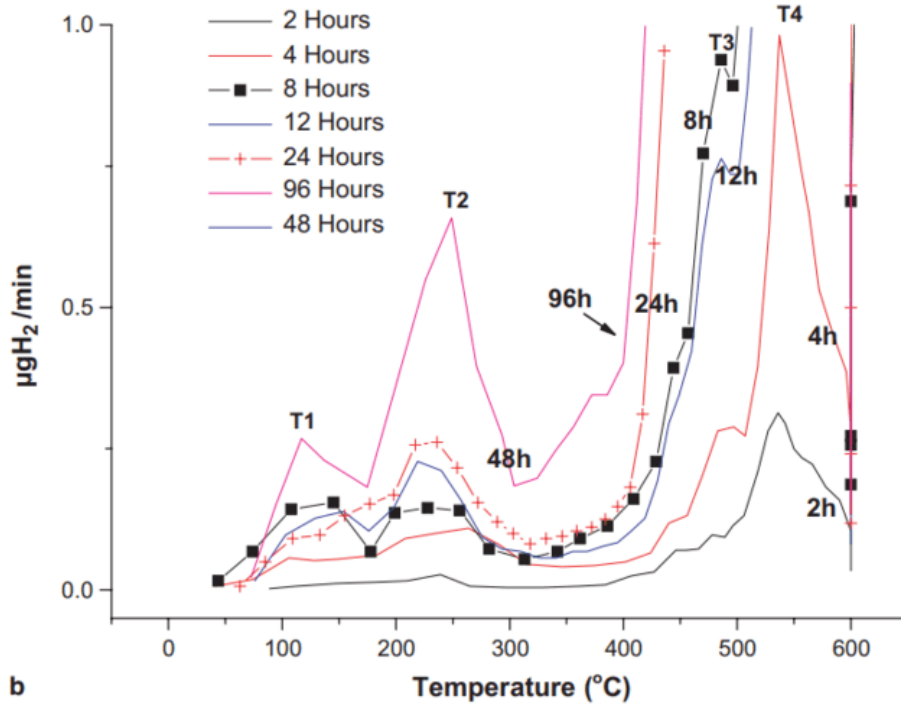


Figure 3-2: T4 peak labeled in the diagram liberates more hydrogen and at a higher temperature than the labeled T2 peak, so it is a stronger trapping site [29]

In general, it should be noted that besides the trapping effect between H and precipitates, hydrogen always interacts with precipitates influencing the structure of the material. In case of coherent precipitates, hydrogen promotes dislocation looping and results in dislocation forest formation with trapped H, which leads to pitting. In contrast, hydrogen interacting with incoherent precipitates promotes slip planarity, and results in intergranular micro-cracks formation because of H to sub-grain and grain boundaries [52]. A more detailed explanation is shown in Fig. 3-3.

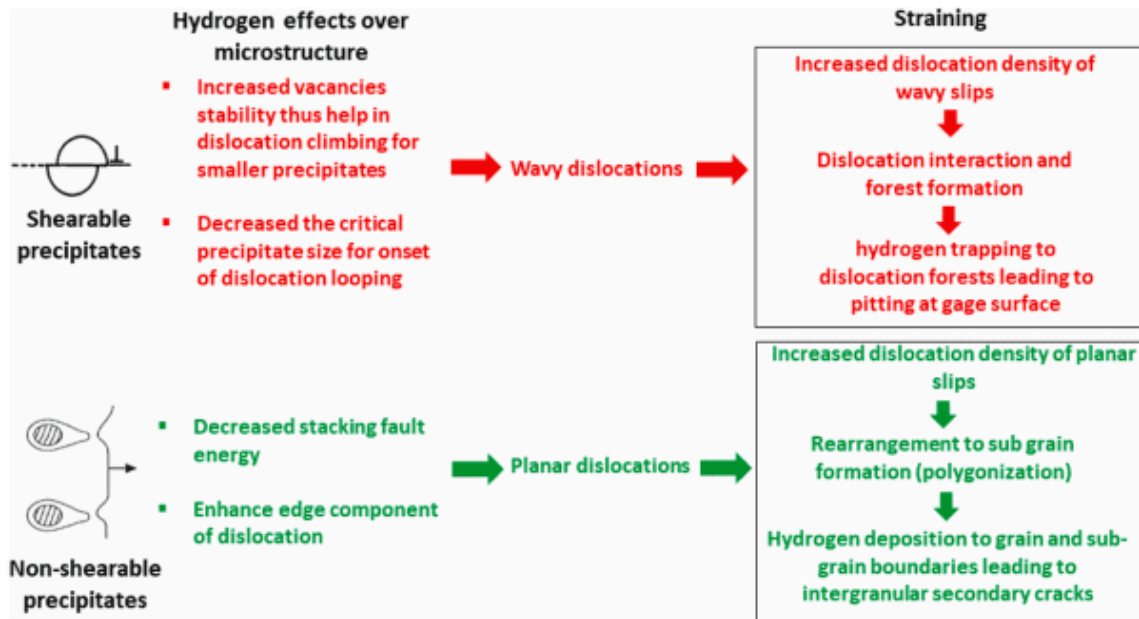


Figure 3-3: Schematic explanation of interaction between shearable (coherent) and non-shearable (incoherent) precipitates [52]

From all the above it is clear that the loss of coherency is related to increase in hydrogen trapping. Partially coherent, with a moderate power and incoherent precipitates, with higher power, can trap hydrogen inside them or at the related interfaces, while coherent precipitates have limited power. However, hydrogen near precipitates interacts with them in all states of coherency leading to degradation. So, the presence of precipitates is generally precarious, but less coherency of precipitates decreases trapping.

3.2 Chemistry

Chemistry of the precipitates shows which are the elements that create the precipitate and at what analogy. The strengthening phases that appear during or after ageing treatment are generally known, as mentioned in chapter 2, and they are determinate for each specific alloy.

For 2xxx Al alloys, Al_2Cu mostly for binary Al-Cu alloys [23,37] and Al_2CuMg for more complicated alloys are the strengthening precipitates. AA 2024 alloy, which is a widely studied alloy may create either one of the above precipitates [8,10,24,33]. Respectively, for 6xxx Al alloys, like 6082 the strengthening precipitates are Mg_2Si [37,51] and for 7xxx in most alloys like 7003,7046,7068,7A99 the strengthening precipitates are $MgZn_2$ [7,12,13,16,50,53]. Phases Mg_2Si , Al_2CuMg and Al_2Cu or other second phases may form inside the alloy in

combination with the main strengthening phase [5,6,8,9,36], as shown in Fig. 3-4, Fig. 3-5 and Fig. 3-6, which can also trap some hydrogen [33]. The specific crystal structure of the precipitates inside the alloy is the same for semi-coherent and equilibrium strengthening phases [8].

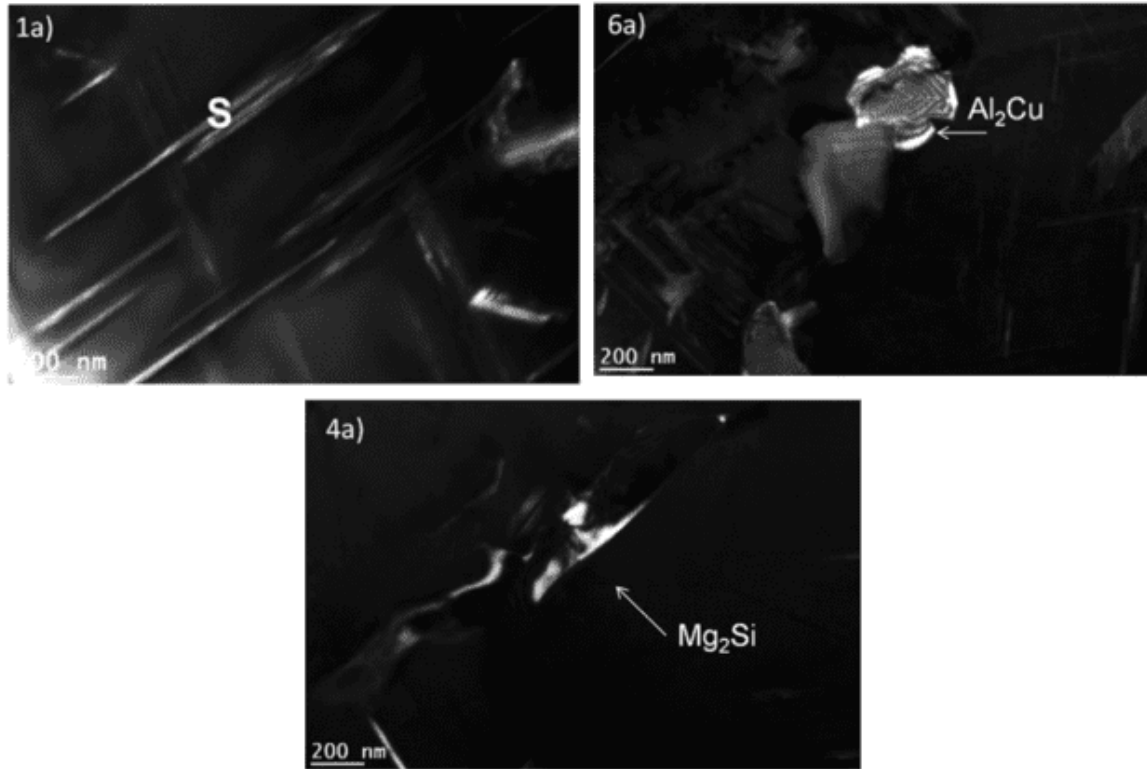


Figure 3-4: TEM micrographs: Al_2Cu - θ phase and Mg_2Si - β phase appear along with the main Al_2CuMg - S phase for AA2024 [8]

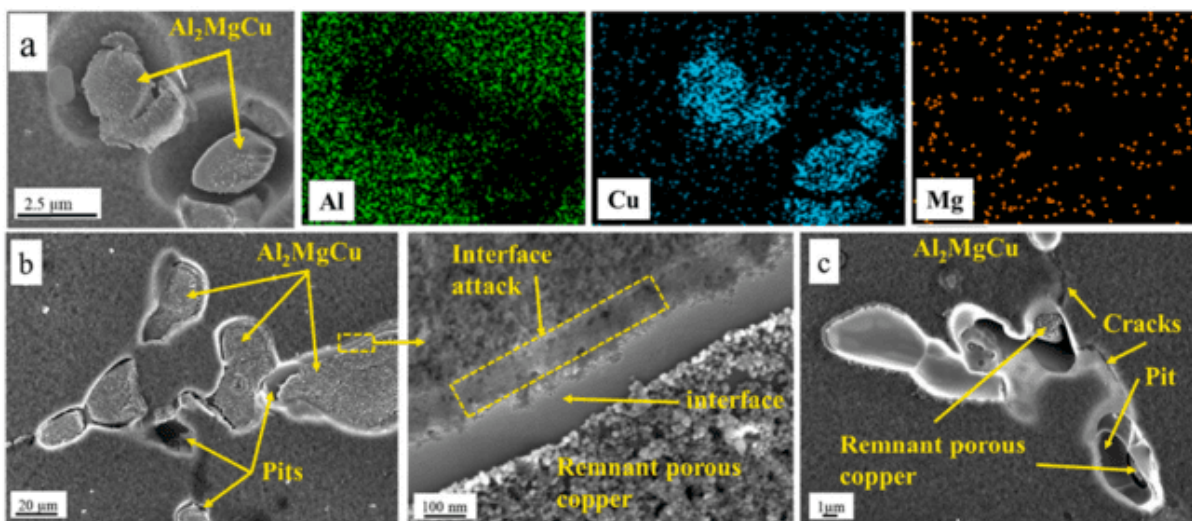


Figure 3-5: EDS element mapping analyses: Al_2CuMg - S phase appear near cracks, tips and interfaces for AA7068 apart from hardening η - MgZn_2 phase [6]

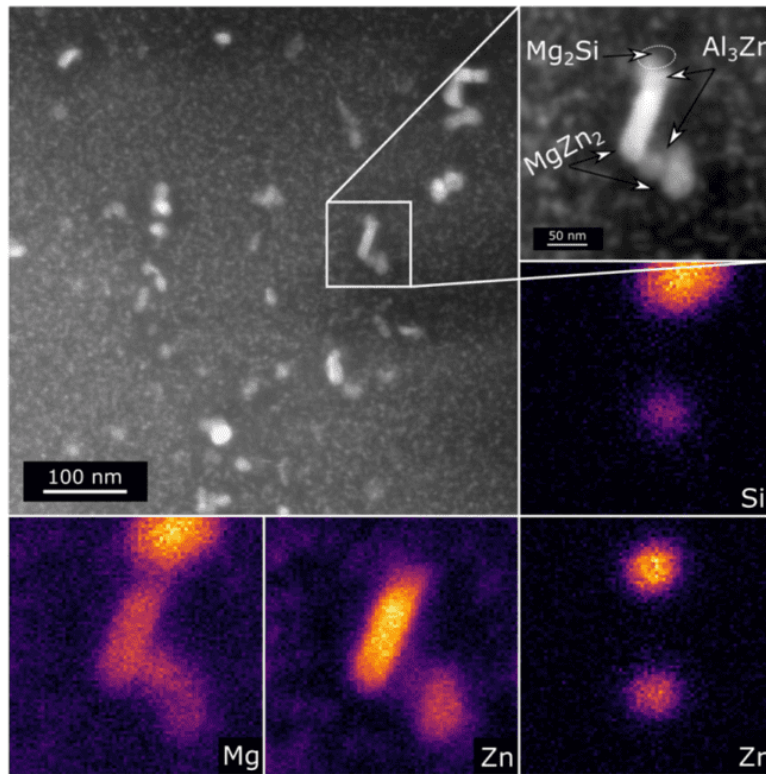


Figure 3-6: HAADF-STEM micrographs: Mg_2Si - β phase appear along with the main $MgZn_2$ η -phase for AA7003 [12]

There are two mentions that may be able to correlate Hydrogen Embrittlement with chemistry of precipitates. Parvizi et al [24], studying 2024 alloy made the observation that for an H-charged condition more atomic hydrogen is trapped in Mg_2Si precipitates than in S-phase or $MnZn_2$ precipitates. Also, Chao and Karnesky [23] present the idea that the presence of Mg-containing S-phase may lead to a lower volume of θ phase inside an Al alloy. Thus, Mg inside an alloy and the creation of the S precipitates affect the θ precipitates and may lead to a different distribution of the trapped hydrogen.

Therefore, regarding chemistry of precipitates there are no proofs in general that a specific chemistry can trap more hydrogen, but there are specified chemistries that form depending on the series of Al alloys. One 2xxx Al alloy, in one experiment showed more hydrogen in β phase instead of η phase or S phase, so this is a first guideline but given the fact that β is not alloys' main hardening phase it may not be very useful. Also, the fact that nucleation of S phase constrains the nucleation of θ phase alters the chemistry that traps hydrogen, but someone should study this situation combined with information about the amount of hydrogen inside θ and S phases.

3.3 Size

Shukla et al [52], studying a 7050 alloy, hydrogen pre-charged and for three different types of microstructures after heat treatment (MA3, MA5, OA), found matrix precipitates sizes 5.4 ± 1 nm for MA3 condition, 7.6 ± 2 nm for MA5 and 13.4 ± 4 nm for OA, as shown in Fig. 3-7. It was found that MA5 specimens can evolve three times higher H evolution than MA3 and that MA5 can trap H more efficiently than OA, due to dislocation forests and planar dislocations that they form respectively. So, it seems that more hydrogen is trapped for 7.6 ± 2 nm precipitates.

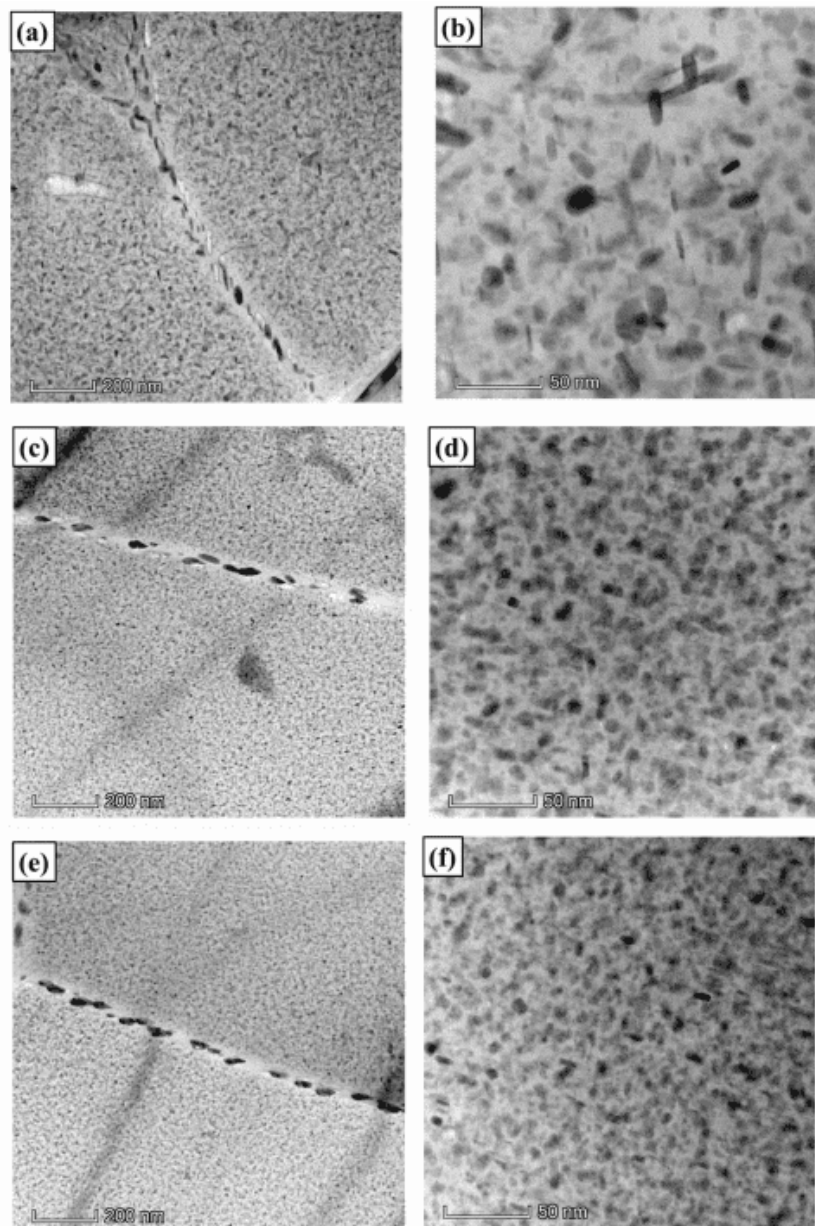


Figure 3-7: Micrographs of a) and b) OA precipitates, c) and d) MA5 precipitates and e) and f) MA3 precipitates. Comparison between the three conditions, gradual reduction of the size from b) to f) [52]

Oger et al [13], showed results for AA7046, charged with hydrogen by cathodic charging and aged at 150 °C. The size of intragranular precipitates was found to reach 6nm after 5h of ageing, 10nm after 20h and 17nm after 48h, as shown in HRTEM micrographs (Fig. 3-8). Also, intergranular precipitates were found to grow from 15 ± 6 nm before ageing (T4) to 61 ± 25 nm at 48h of ageing, as shown in TEM micrographs (Fig. 3-9). Study revealed that until 5h of ageing the hardening precipitates (GP zones and η') were associated with stress fields of the lattice and thus the quantity of trapped hydrogen was limited, whereas between 5h and 20h of ageing precipitates coalesced, the total length of precipitates-matrix interface increased and therefore more hydrogen was trapped. Also, during the ageing from 20h to 48h the size of precipitates did not affect the hydrogen trapping. As a result, the size of precipitates affects H trapping until 20h of ageing and the bigger size after 5h of ageing allows precipitates to be more susceptible to trapping. So, for intragranular precipitates, size between 6 nm and 10 nm make them prone to hydrogen accumulation, whereas for intergranular precipitates bigger than 21 nm (for the maximum size before ageing) end smaller than 36 nm (before they reach minimum size for 48h) size lead to H trapping.

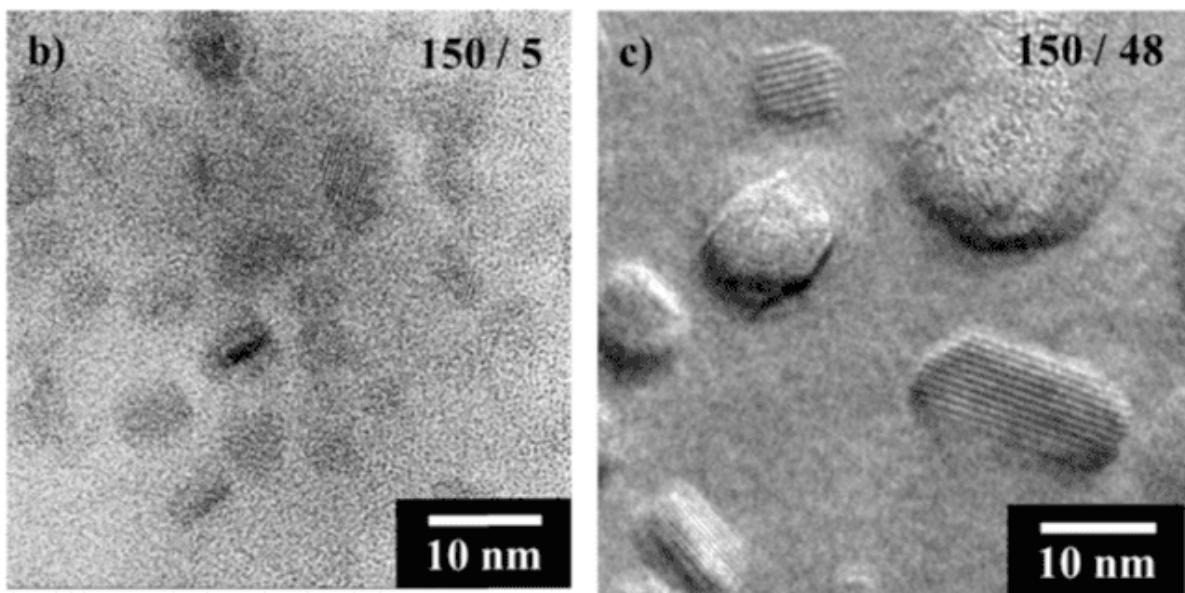


Figure 3-8: HRTEM micrographs: Left) η' intragranular precipitates after 5h and right) η intragranular precipitates after 48h [13]

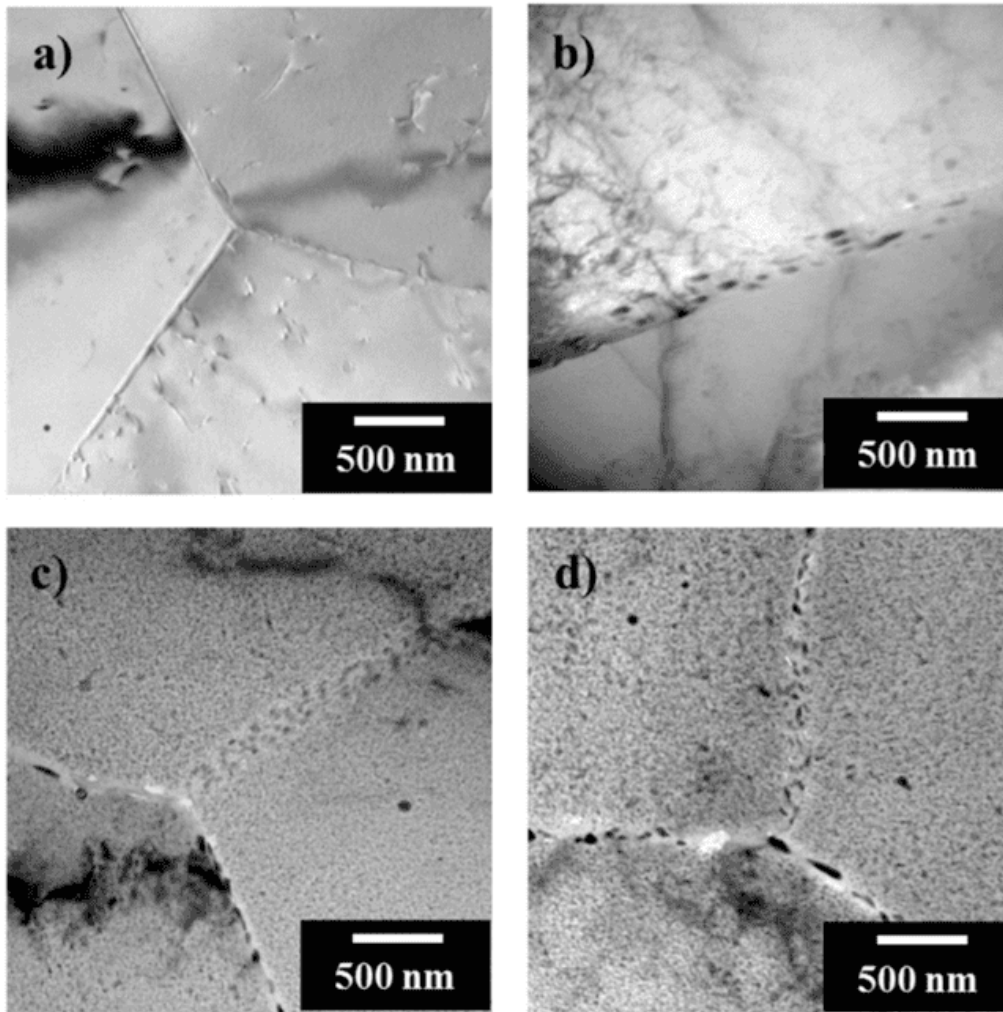


Figure 3-9: TEM micrographs: intergranular precipitates a) before ageing, b) after 5h of ageing, c) after 20h of ageing and d) after 48h of ageing [13]

Chen et al [54], reported presence of precipitates both inside the grains and at the grain boundaries for a 7xxx Al alloy. TEM results, as shown in Fig. 3-10, identified the sizes of the intragranular precipitates for the natural-aged (NA), peak-aged (PA) and over-aged (OA) conditions. Coherent GP zones 3.2 ± 0.4 nm, η' precipitates 4.5 ± 0.5 nm and η precipitates 14.3 ± 2.5 nm were measured for each condition, respectively. The study showed that OA condition present a much better HE resistance than NA and PA conditions, based on the elongation loss and on the number density of cracks, during hydrogen charging. There was a big elongation loss (43.4% and 20.6%) for NA and PA conditions whereas for OA condition elongation loss was only 1.7%, as shown in Fig. 3-11. Also, the increase in density of cracks was around 43 mm^{-2} for NA, around 40 mm^{-2} for PA and only around 15 mm^{-2} for OA condition, as shown in Fig. 3-12, hence hydrogen does not seem to influence significant the alloy at the

OA condition. So, intragranular precipitates with sizes smaller than 11.6 nm (14.3-2.5) and larger than 3.6 nm (3.2+0.4) may be more prone to hydrogen-induced damage.

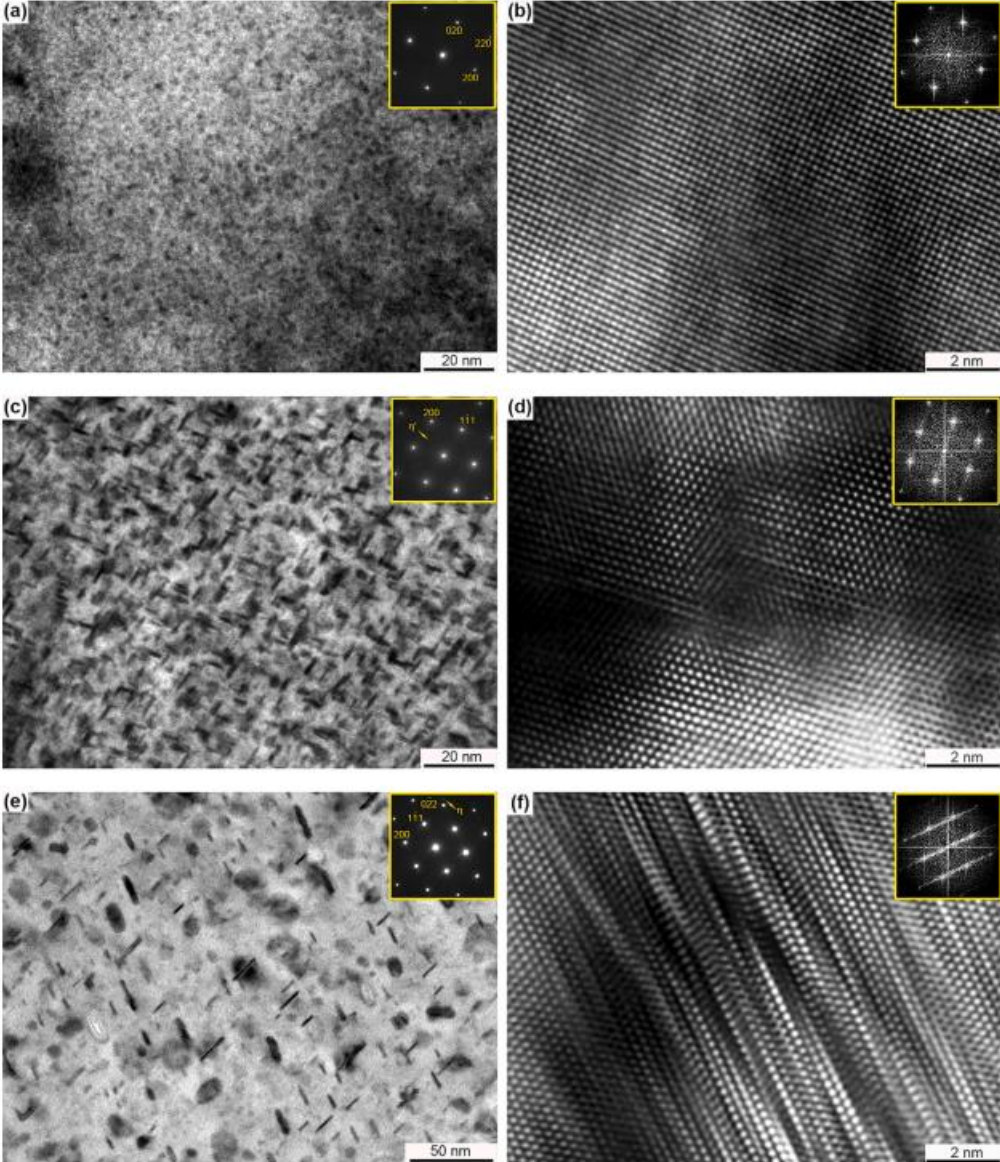


Figure 3-10: TEM micrographs of a) NA, c) PA and e) OA samples and HRTEM micrographs of b) NA, d) PA and f) OA samples [54]

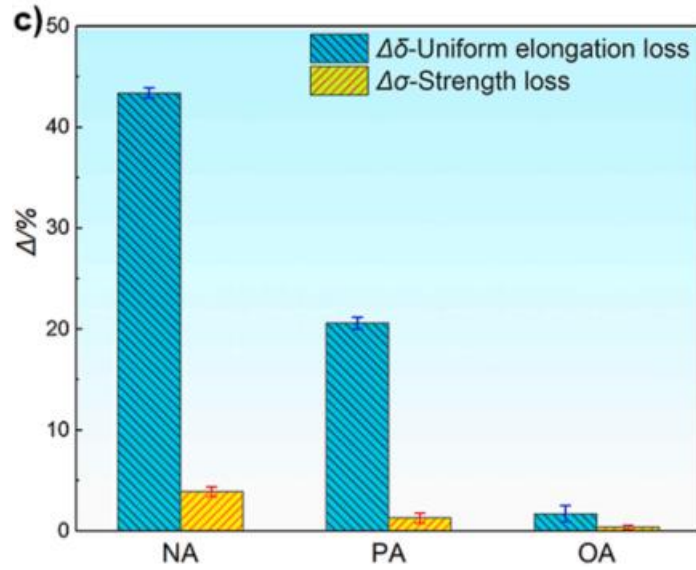


Figure 3-11: diagram shows elongation loss (blue columns) for NA, PA and OA conditions [54]

Statistical results of crack number density and A_0/A_m near fracture surface.

Sample	Silicone oil		In-situ hydrogen charging	
	Number density (mm^{-2})	A_0/A_m	Number density (mm^{-2})	A_0/A_m
NA	10.3 ± 0.5	1.22 ± 0.12	53.6 ± 2.9	1.11 ± 0.18
PA	5.7 ± 0.8	1.23 ± 0.18	45.2 ± 1.8	1.19 ± 0.22
OA	0.6 ± 0.2	1.86 ± 0.23	15.6 ± 2.2	1.85 ± 0.12

Figure 3-12: Data for cracks number density for NA, PA and OA conditions [54]

At the work of Alexopoulos et al. [36], AA 2024 alloy specimens were exposed to hydrogen and aged treated at different ageing temperatures and the experiments showed evidence of ductility decrease related to hydrogen from corrosion, as mentioned in chapter 2 and as shown above in Fig. 2-1. Initial ductility degradation at pre-treated condition (around 26%) decreased during under-ageing and the less ductility decrease was shown at peak-ageing condition (around 11%). Moreover, from peak-ageing to over-ageing ductility decrease was restored and reached almost its initial value (around 22%). It is also reported that S precipitates (the hardening phase) have thicknesses less than around 3nm before heat treatment and at the under-ageing, thicknesses from around 3nm to around 8nm at the peak-ageing and are thicker than 8nm at over-ageing. Subsequently, due to lower degradation of

alloy's ductility it seems that a better resistance to Hydrogen Embrittlement may be achieved for precipitates with thicknesses between 3nm and 8nm.

Hou et al [7], studying 7A99 Al alloy noticed that for precipitates along grain boundaries, for the over-aged condition, are larger than 25 nm, as shown in Fig. 3-13, and act as hydrogen trapping sites. They state that 25nm is a critical size, because precipitates larger than this can act as irreversible trapping sites for atomic H.

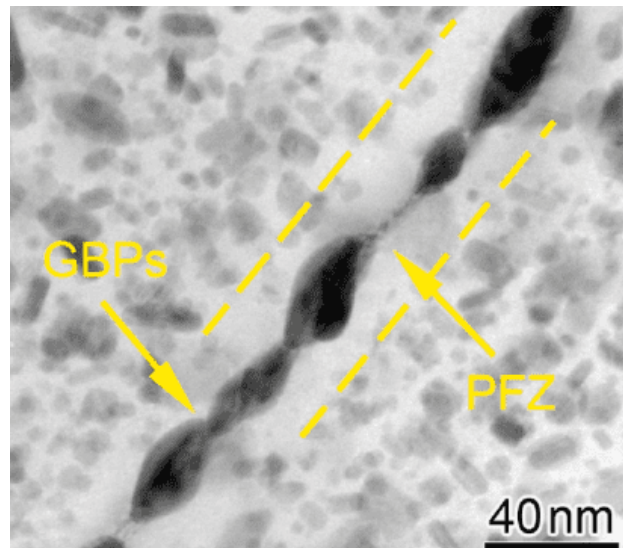


Figure 3-13: TEM micrograph of grain boundary precipitates of AA7A99 [7]

An older publication from Iijima et al. [50], for an Al-6wt% Zn-2wt% Mg alloy, which belongs to the 7xxx series, says that with the growth of over-aged η precipitates the trapping power decreases in comparison with the power of smaller η precipitates. So, coarsening of these precipitates after they reach their equilibrium phase no more affect H trapping.

Kumar et al [6], mentioned that large grain boundary precipitates, which cause larger inter-precipitate distance, trap more atomic hydrogen leading to formation of molecular hydrogen. This effect reduces the concentration of the atomic hydrogen near the precipitates and thus the possibility of its diffusion and trapping.

As a result, for 7xxx Al alloys, precipitates inside the grains should not have sizes between 4.6 ± 1 nm and 10.6 ± 1 nm, while precipitates at the grain boundaries should not have sizes between 23 ± 2 nm and 36nm. Precipitates larger than the upper limit that is presented are found to not have trapping power, because generally coarser precipitates are not prone to atomic H adsorption. Moreover, for 2xxx Al alloys should have thicknesses

around 3nm and 8 nm, in order to lower ductility decrease. These suggestions are studied for a specific series, but they can be applied for all precipitation hardening Al alloys as a base.

3.4 Morphology

In regard to the morphology of precipitates and its interaction with the hydrogen trapping there is no direct linking. Some studies contain information about the morphology of some precipitates and this information can be combined with information about which precipitates trap more hydrogen.

For Al-Cu alloy GPI zones are layers of Cu, GPII zones two layers of Cu between three planes of Al, θ' have a plate-like morphology and a body-centered tetragonal crystal structure and θ have granular morphology and a tetragonal C16 crystal structure [37,55]. Moreover, β' precipitates are considered rod-like and β plate-like [37], as shown in Fig. 3-14, and S-phase precipitates are round [36]. For 7xxx Al alloys GP zones are spherical, η' needle-like particles and η lath-like particles [53], as shown in Fig. 3-15 and Fig. 3-16.

So, according to what is mentioned in section 3.1, hydrogen is more possible to be trapped at C16 tetragonal crystal structure rather than body-centered tetragonal crystal structure. Also, it is more possible to be trapped at granular θ precipitates rather than plate-like θ' precipitates, plate-like β precipitates rather than rod-like β' precipitates and at lath-like η precipitates rather than needle-like η' precipitates. Moreover, the round S-phase precipitates seem to have a high trapping power, because they are a high energy T4 trapping site.

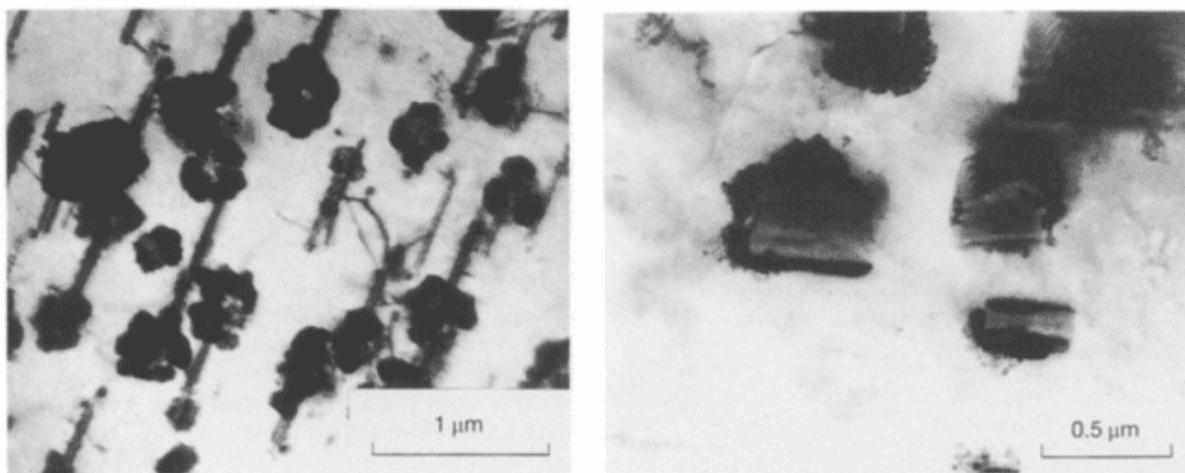


Figure 3-14: Tritium EM autoradiographs: left) β' precipitates and right) β precipitates [37]

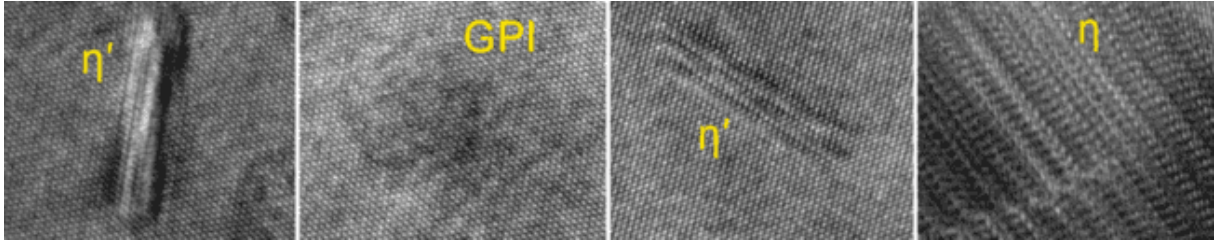


Figure 3-15: HRTEM images: GPI zones, η' precipitates and η precipitates for 7A99 [7]

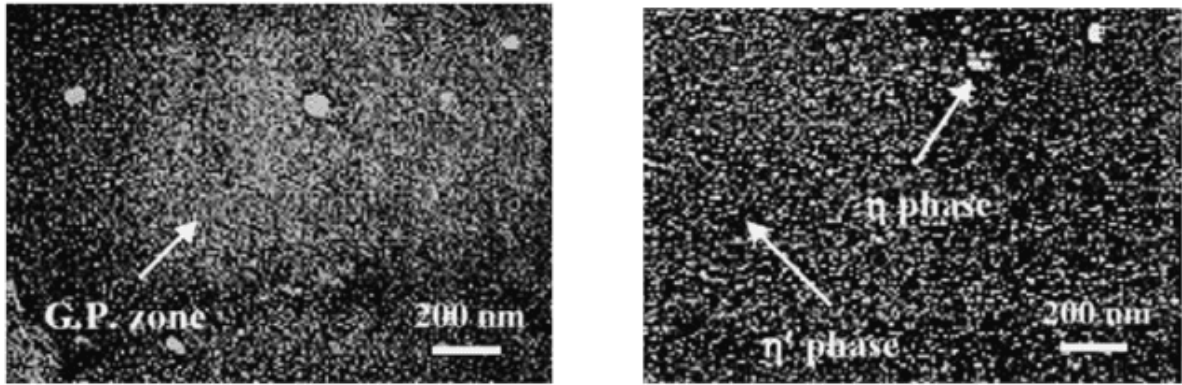


Figure 3-16: TEM micrographs: left) GP zones of AA7175 and right) η' and η precipitates for AA7175 [53]

Chapter 4. Interaction between precipitates and defects, features, environment or treatment

Apart from all the above, attention should be given to defects and features of microstructure and to the treatment parameters of the precipitation hardening Al-alloy. Many publications mention that there is correlation between heat treatment, loading parameters, temperature, the service or testing environment, the time, the matrix and HE [11,14,17,34,35]. Simultaneously, the final form, state and quantity of precipitates are strongly depended on treatment, environment and microstructural features. As a result, it is essential to analyze the potential influence of each of the below parameters to the condition of the precipitates during the presence of hydrogen.

4.1 Dislocations

First of all, research show that dislocations are possible trap sites for hydrogen at 7xxx Al alloys, and as mentioned in chapter 2 generally for precipitation hardening alloys [14,32,50]. Hence, the fact that there are dislocations inside an alloy may lead to less hydrogen trapped around or inside precipitates because of the existence of an alternative trapping site. Su et al [32], state that H is mainly trapped at edge dislocations instead of screw dislocations. Moreover, it is affirmed that dislocations in many cases act as short-circuiting diffusion paths [14,37,50], easier way for H atoms to be transported inside the grain. At the same time, the ingress of hydrogen in a material improves dislocation mobility and facilitates dislocation emission from the crack tips [14,25]. This situation combined with the fact that dislocations are diffusion paths could affect how easy hydrogen reaches matrix precipitates.

Secondly, the most obvious relationship between dislocations and precipitates has to do with the formation and the development of dislocations due to precipitates. Semi-coherent and incoherent precipitates increase the density of dislocations around them by misfit dislocations due to the precipitate/matrix interface and by generating them due to different thermal expansion coefficients between matrix and precipitates [23]. These dislocations can trap hydrogen and accumulate it near the interface of the precipitates [37]. The strain dipoles and the misfit dislocations at the matrix are sometimes a way to identify the state of coherency for precipitates [10].

Lastly, it is worth mentioning that in the presence of hydrogen the behavior of dislocations is opposite for coherent and incoherent precipitates [52]. If precipitates are coherent, dislocations looping is easier because hydrogen decreases the vacancy formation energy and force dislocations to bow or climb around precipitates. This ends up in formation of dislocation forest which traps H and enhances pitting. Contrary to the above wavy dislocations, for incoherent precipitates dislocations undergo planar slip, during increasing strain, because hydrogen reduce the probability of cross slip. This slip planarity promotes hydrogen transport to boundaries, which cause micro-cracks formation. However, besides the different mechanisms, it is clear that dislocations near precipitates in the presence of hydrogen have negative effect for the material, causing H-related degradation.

Studying dislocations bring the conclusion that their relationship with precipitates is complex, but generally precipitates end up having more hydrogen around them due to dislocations, and a useful way to exploit dislocations is to use them as medium-energy trapping sites for hydrogen.

4.2 Grain Boundaries

The main ways that grain boundaries could affect the trapping of hydrogen at the precipitates and the Hydrogen Embrittlement of a precipitation hardening Al alloy are already mentioned above, in chapter 2. It is reported that grain boundaries are a possible but weak H trapping site for 7xxx Al alloys [14,32], as shown in Fig. 4-1, and also that they act as short-circuiting diffusion path for H [37]. Older and more recent publications for several precipitation hardening Al alloys (alloys containing Cu or Mg_2Si phase [37] and alloys containing Zn and Mg [32,50]) show that grain boundaries have low or nearly zero, in some alloys, trapping power, as shown in Fig. 4-2, so they should not be a concerning microstructure defect for HE. Simultaneously, grain boundaries' ability to let hydrogen diffuse easier and faster [37] may be worrying depending on where H ends up. Hydrogen can, in this way, reach energetically favored trapping sites and affect properties of the material or it can reach and propagate crack tips and accumulated strains, resulting in premature H-induced failure, during service time. Moreover, presence of hydrogen along grain boundaries causes grain boundary cracks, which may result in grain boundary fracture [18,53]. Lastly, it should be mentioned that Su et al [32], comment that grain boundaries have higher binding energy with hydrogen than lath boundaries or precipitates.

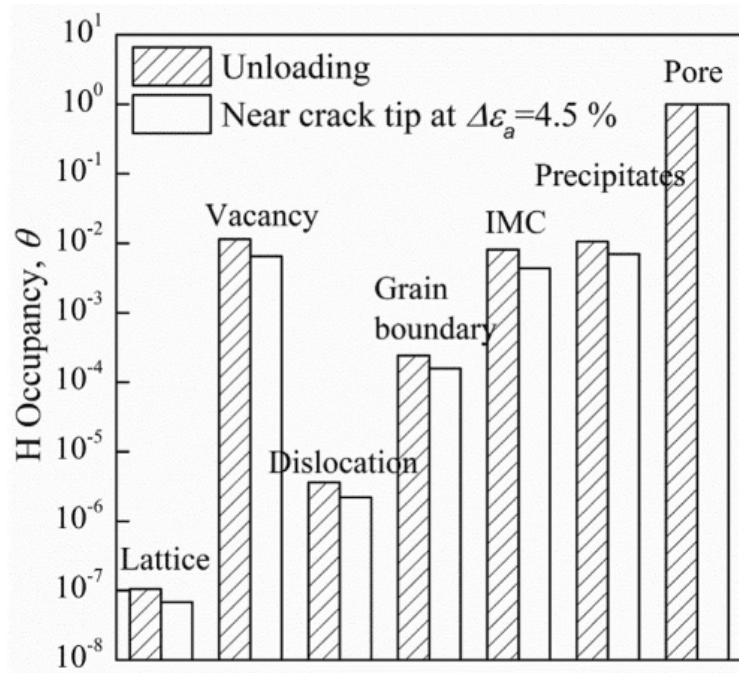


Figure 4-1: Diagram showing grain boundaries' trapping power for hydrogen for 7xxx Al alloy [32]

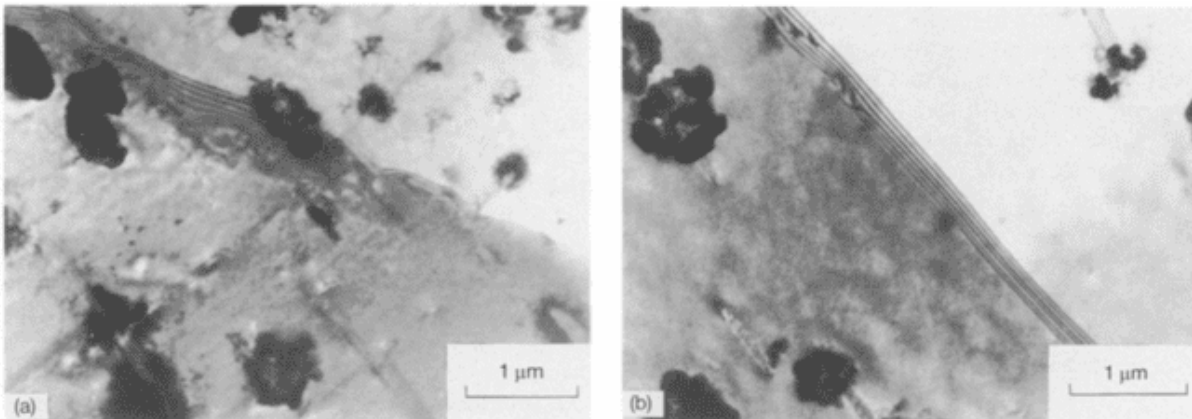


Figure 4-2: Tritium EM autoradiographs: a) grain boundaries with precipitates (for Al-1% Mg₂Si alloy) have silver grains, that indicate hydrogen, at the interface while b) grain boundaries without precipitates have no silver grains [37]

Concurrently, grain boundaries inside a material seem to be preferential sites for precipitates to be created and grow. There are multiple mentions for grain boundary precipitates (GBPs) [5,6,36], that can trap hydrogen, as shown in Fig. 4-3. These GBPs seem to be coarser than matrix precipitates, around 20-50 nm [5], and it is stated that larger GBP can result in the formation of molecular hydrogen (from atomic H trapped) due to more space [6], or enhance HE resistance [54]. The size of these GBP may be inside the range of the susceptible precipitate sizes mentioned for intergranular precipitates in section 3.3 above, and hence

these grain boundary precipitates may trap hydrogen, but it is possible to not maintain dangerous atomic H.

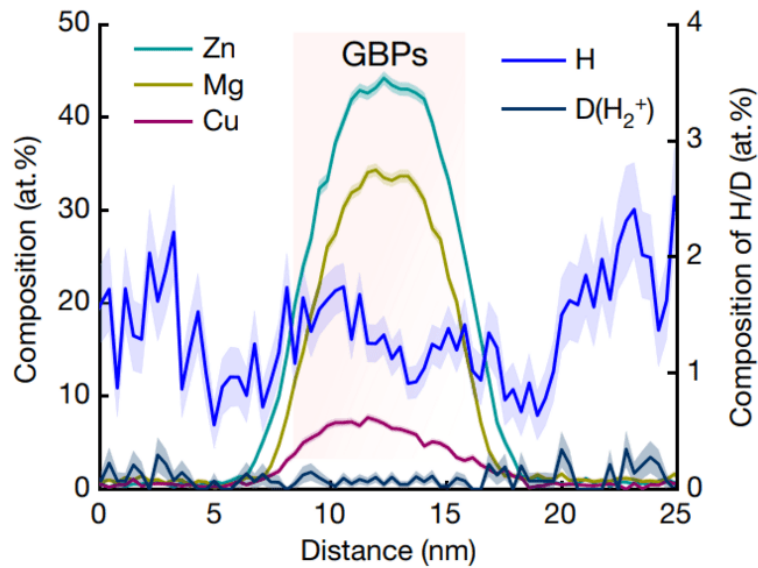


Figure 4-3: H amount at GBPs [5]

To sum up, grain boundaries play a controversial role for H-induced degradation for precipitation hardening alloys, because they can increase hydrogen diffusion rate, so they are not wanted during H diffusion. However, precipitates can nucleate at grain boundaries and these precipitates are generally less prone to H trapping due to their size. Hence, grain boundaries quantity and locations should be controlled as much as possible.

4.3 Vacancies

There is no direct correlation between vacancies, precipitates and their susceptibility to trap hydrogen. In chapter 2, it was reported that vacancies are sites of microstructure that trap hydrogen. For pure Al and 7xxx Al alloys, vacancies are referred as high energy H trapping sites, and 2xxx Al alloys research mentions them as trapping sites [4], so it can be assumed that H may be trapped in vacancies for all precipitation hardening alloys. This assumption is logical also because precipitation hardening alloys are heat treated and after quench there are many frozen-in vacancies [15], which attract hydrogen to be trapped due to high binding enthalpy [53]. Moreover, it is known that hydrogen improves stability of vacancies by decreasing the vacancy formation energy [52], and that the presence of strain localization regions increases the density of vacancies [17], hence it is clear that the interaction between vacancies and hydrogen is unavoidable.

Another noteworthy relationship between Hydrogen Embrittlement and vacancies is, as analyzed in chapter 2, that vacancies are a key parameter for a HE mechanism (HESIV). It is previously mentioned that HESIV is a possible mechanism for Al alloys because Al has a low energy for vacancy formation, and thus Al alloys with more vacancies are more susceptible to it. This mechanism uses vacancies and solute H to create vacancy-H complexes and eventually vacancy-H clusters which limit dislocation emission from the crack tip [40,43]. So, to prevent this from happening someone should try minimizing the vacancies in the material, or at least try keep them away from vulnerable sites.

The only hopeful information that there is regarding vacancies is a result that Kamoutsi et al [15] came up with, studying a 2024 Al alloy. In their experiment, for exposure time in a corrosive solution, bigger than 12h more annealing out of thermal vacancies was observed (compared with after 6h exposure), and hence less hydrogen was trapped in those specimens. As a result, annealing could be a way to adjust the vacancies inside the precipitation hardening alloy.

4.4 Dispersoids

Dispersoids are particles of second phases, which form during homogenization, so they are present during the heat treatment of precipitation hardening Al alloys and the creation of precipitates [56]. Some previous studies showed that dispersoids may affect the nucleation and growth of precipitates or the H adsorption and trapping.

A study for AA 7150 alloy, which is a 7xxx alloy with Zr additions, revealed that the Al_3Zr dispersoids that exist, are possible nucleation site for precipitates [9]. TEM observations showed that the incoherent equilibrium dispersoids or the metastable dispersoids after recrystallisation and loss of their coherency act as nucleation sites, at slow cooling conditions. It is found that Al_3Zr dispersoid maintains its orientation and structure during cooling and therefore it can lose its coherency the be a preferred nucleation site for quenched-induced precipitates. Moreover, as shown in Fig. 4-4, TEM experiment revealed that dispersoids in recrystallized grains are more preferential sites for precipitates nucleation than dispersoids in sub-grains. At the same time, Zhao et al [5], mentioned that there is H inside Al_3Zr dispersoid.

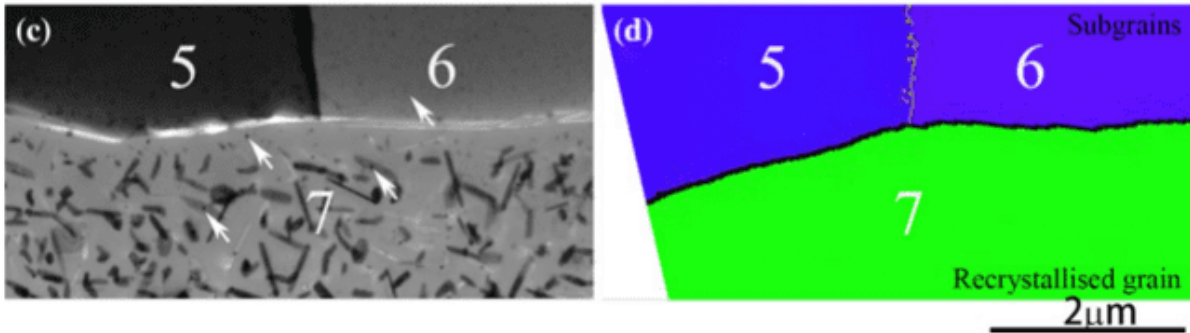


Figure 4-4: TEM: Dispersoids (shown with arrows) trapping for grain and sub-grain [9]

In addition, an atom probe tomography (APT) study for AA 2024 alloy, presented the $\text{Al}_{20}\text{Mn}_3\text{Cu}_2$ dispersoid particles and their interaction with precipitates and hydrogen [24]. S-phase is found to nucleate at the dispersoid interface, and after its growth S-phase shares a boundary with the dispersoid particle which may also serve as a nucleation site. The $\text{Al}_{20}\text{Mn}_3\text{Cu}_2$ dispersoid can trap hydrogen throughout its volume and since it is noted that hydrogen is associated with Mn-rich particles, as shown in Fig. 4-5, it can be implied that dispersoid interface may be a more possible trapping site than other microstructural defects. Moreover, S-phase and S-phase/matrix interface are reported to be trapping sites. Therefore, the fact that S-phase appear near dispersoids and that both dispersoids and precipitates accumulate and trap hydrogen makes the presence of dispersoids at 2024 Al alloys and potentially at all 2xxx alloys a controversial factor for HE.

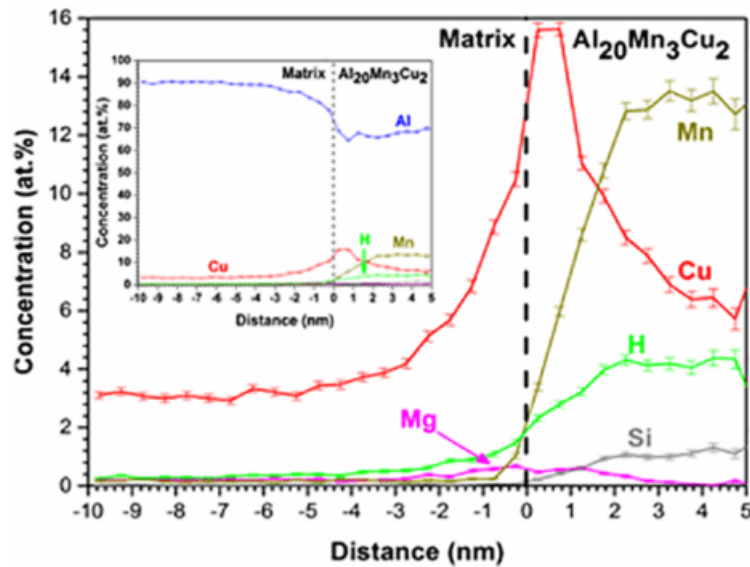


Figure 4-5: Mn and H related at the interface between matrix and dispersoid (dashed line) [24]

All the results about dispersoids conclude to direct interaction between dispersoids, precipitates and the appearance of more interfaces, which can trap hydrogen near precipitate. This situation is not favorable for Al alloys because it inserts many uncertainties for hydrogen trapping.

4.5 Alloying Elements

Alloying elements of an Al alloy are important because specific precipitation phases form depending on the elements, the elements contribute to precipitation [4], some elements may interact with other features of the microstructure that affect precipitation or H trapping and some may influence the hydrogen inside the material.

Firstly, Cu, Mg and Si, and Zn are the characteristic elements for series 2xxx, 6xxx and 7xxx, respectively, as shown in chapter 2. For 2xxx, a representative example of how elements affect precipitation is that there are two main precipitation sequences, and θ precipitates which contain only Al and Cu can nucleate not only for binary alloys but for more complex alloys as well. Also, S and η precipitates need presence of Mg to form, which may imply that Mg is an important element.

In addition, a TDS observation for a 2xxx alloy [23], shows that increasing of the Cu content increases the peak area for precipitates trap and the amount of Deuterium (equivalent with hydrogen in real conditions) for precipitates peak. So, in general it seems that Cu for 2xxx alloys can make the energetically favored trap site stronger and consequently make the alloy more susceptible to HE.

Moreover, as mentioned in section 4.4, dispersoids are important because they influence precipitation and H accumulation. For 2xxx Al alloys, Mn-rich dispersoids are linked with large amounts of hydrogen and increase in Mn profile at the dispersoids decreases Cu-particles (which may be θ precipitates) segregation at the interface of the dispersoid [24]. For 7xxx Al alloys, Zr additions lead to Zr-rich dispersoids, which are found to be dispersoids that promote precipitation. Thus, the desirable amount of Mn and Zr for precipitation hardening alloys should be decided regarding the desirable fraction of precipitates and the location of hydrogen.

Also, a work about 7xxx Al alloys, which introduces intermetallic compound particles as features that increase HE resistance, mentioned Mn additions as favorable [57]. It is stated

that the Al alloy with Mn, overcomes the decrease of ductility due to hydrogen and that Mn-added alloys enhance the resistance of HE, as shown in Fig. 4-6.

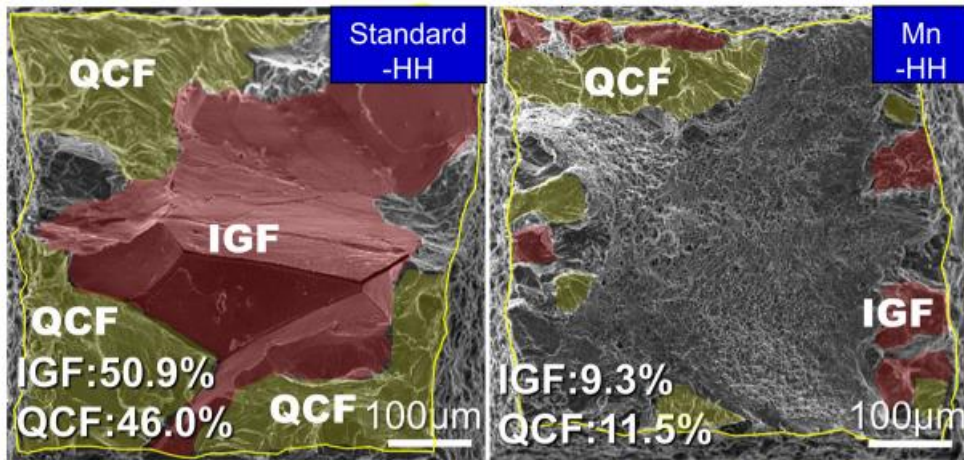


Figure 4-6: Fracture morphology of Al alloy (left) standard alloy (right) alloy with Mn addition [57]

Furthermore, many publications point out the dangerous nature of Mg for Hydrogen Embrittlement since it affects hydrogen. Presence of Mg increases solubility of hydrogen [4] and Mg segregation improves H adsorption [5]. Co-segregation of Mg-H leads to H-induced degradation of the alloy, as there are reports for Hydrogen Induced Cracking and Hydrogen Embrittlement [5,7]. The binding energy between Mg and H in Al is strong [4,16] and a result from Tsuru et al [16], that when H interstitial sites surrounded by two Mg and two Zn atoms are stable and when they are surrounded by one Mg and two Zn are unstable enhances the assumption that H bubbles nucleate at regions with Mg. However, Mg segregation at grain boundaries is reported to decrease while ageing time increases [53].

Also, in a study it is presented that there are Fe and Si impurities because of the low solubility of these atoms for Al-Mg alloys [8], and for 7xxx it is reported that presence of Fe and Si at an alloy with hydrogen decreases fracture strain and low Fe, Si content leads to less micropores [32]. Hence, there is a possibility that control of Fe and Si for alloys that contain Mg can help in the resistance for HE.

Lastly, among other alloying elements it is noted that Li, Sc, Ti and Co have strong binding energies with hydrogen in Al [4] and that Zn atoms do not tend to trap hydrogen around them [16].

4.6 Crack Tips

Crack tips are generally an unwanted defect of microstructure for a material because they destroy the uniformity of it. Crack tips disrupt the crystal structure and hence affect the distribution of the matrix, the anisotropy, the stress fields and many mechanical properties. They, also get involved in some HE mechanisms, as they are sites where the initiation or the propagation of crack and fracture happens [6]. Hydrogen from environment can reach crack tips easily, and the presence of H at the crack tips provokes dislocations and vacancies emission and multiplication and dislocations mobility [25,32].

4.7 Heat Treatment

The two main parameters of heat treatment, the ageing temperature and the ageing time, impact on the precipitation and the hydrogen concentration when the material is exposed to hydrogen environment. Precipitates nucleate and grow during heat treatment, their coherency is based on the parameters of the ageing and the state of coherency is time-dependent during exposure to a certain temperature [10,36]. So, depending on the desirable coherency there is a different treatment. At the same time, thermal activation of an alloy with trapped H, leads to desorption of hydrogen at a certain temperature from each trap site [8]. The same idea is the base of TDS experiments, mentioned in chapter 2, but heating in a high temperature can be used for materials to lower H content.

It is reported that a large amount of S-phase and a faster growth of a precipitation phase for 7175 Al alloy is achieved for higher temperatures of ageing [8,53], but for Al-Cu alloys ageing between 300 °C and 500 °C may lead to dissolution of precipitates [23]. Also, the precipitation sequence does not seem to alter with ageing at higher temperature [53]. A well distributed, balanced and stabilized formation of coherent and subsequently incoherent precipitates was achieved for lower temperatures, as reported in a study [36]. However, the same study points out that well-distributed particles triple the pitting potential, so this kind of formation may not be beneficial. Moreover, it should be noted that for temperatures above solvus of GP zones, these zones do not form during ageing and they do not consist a trapping site [10].

There are multiple sources which state that hydrogen concentration is influenced by ageing time and temperature, and since heat treatment is necessary for precipitation someone should focus on the emergence of hydrogen during it. For 2xxx Al alloys experiments

show that during ageing H content increases with time, as shown in Fig. 4-7. In addition, it is reported that for ageing times up to 9h, increasing of time decreases corrosion resistance [10], and thus more hydrogen will be released from corrosion. For 7175 Al alloy, study revealed that H concentration decreases with increasing ageing time [53], because excess vacancies are mentioned as the main trap site and these become fewer with time. So, most of the mentions about hydrogen lead to the conclusion that more hydrogen may occur with more time, but depending on the strong trapping sites this hydrogen may or may not accumulate inside the material.

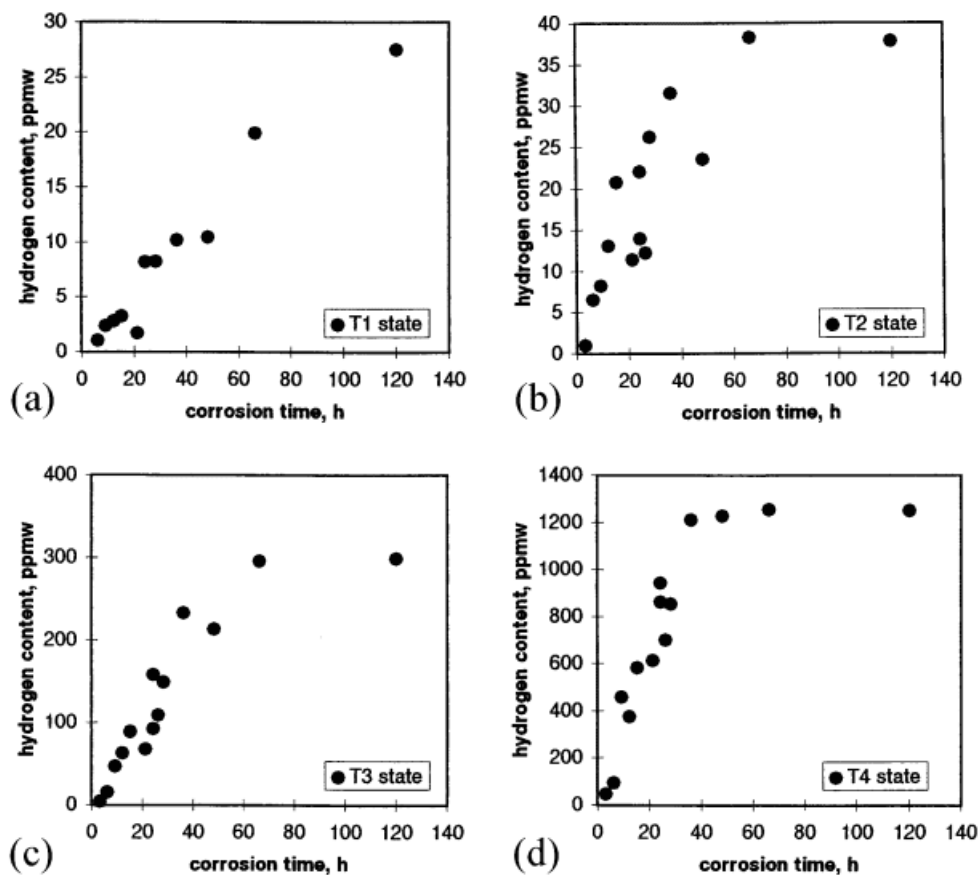


Figure 4-7: Hydrogen content at four different trapping sites in regard with corrosion time for AA2024 [33]

In regard with ductility decrease for exposed to corrosion-related hydrogen AA 2024 alloys, least decrease is observed for lower temperature and for times around peak-ageing [36]. The decrease was higher for over-ageing times, as shown in Fig. 4-8.

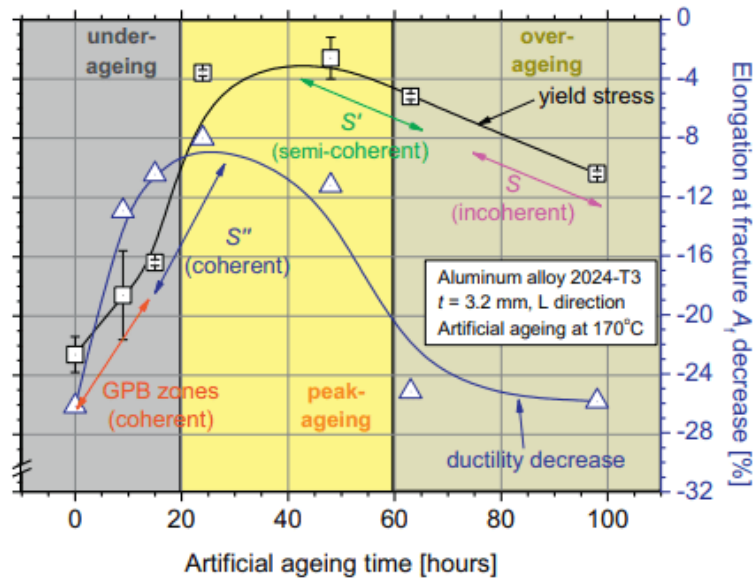


Figure 4-8: Curve for ductility decrease on the diagram, the highest decrease inside over-ageing area [36]

Consequently, temperature during heat treatment is generally certain and alters depending on the wanted microstructure. However, within the allowed limits it should not be very high because dissolution of precipitates and hydrogen liberation may happen and it should not be very low because the resulting distribution is not useful. Furthermore, ageing time during heat treatment should be relatively short for 2xxx Al alloys that trap hydrogen at precipitates, but it should be longer for 7xxx Al alloys that trap hydrogen at vacancies.

4.8 Strain – Deformations

Strain or deformation of a material, prior or during hydrogen exposure, leads to changes of the matrix and the general structure of an alloy. Plastic deformation prior to corrosion or increase in applied strain levels are reported to cause decrease of H diffusivity and H content at the trapping site of precipitates [15,32]. These observations are shown for 2xxx and 7xxx Al alloys, respectively, and Fig. 4-9 and Fig. 4-10 show the reduction of trapped hydrogen at precipitates trap sites for strains above 0,06 and for 4,5% strain levels, for each experiment. For the 7xxx Al alloy researchers observed that precipitates remain a main trapping site, as shown in Fig. 4-9.

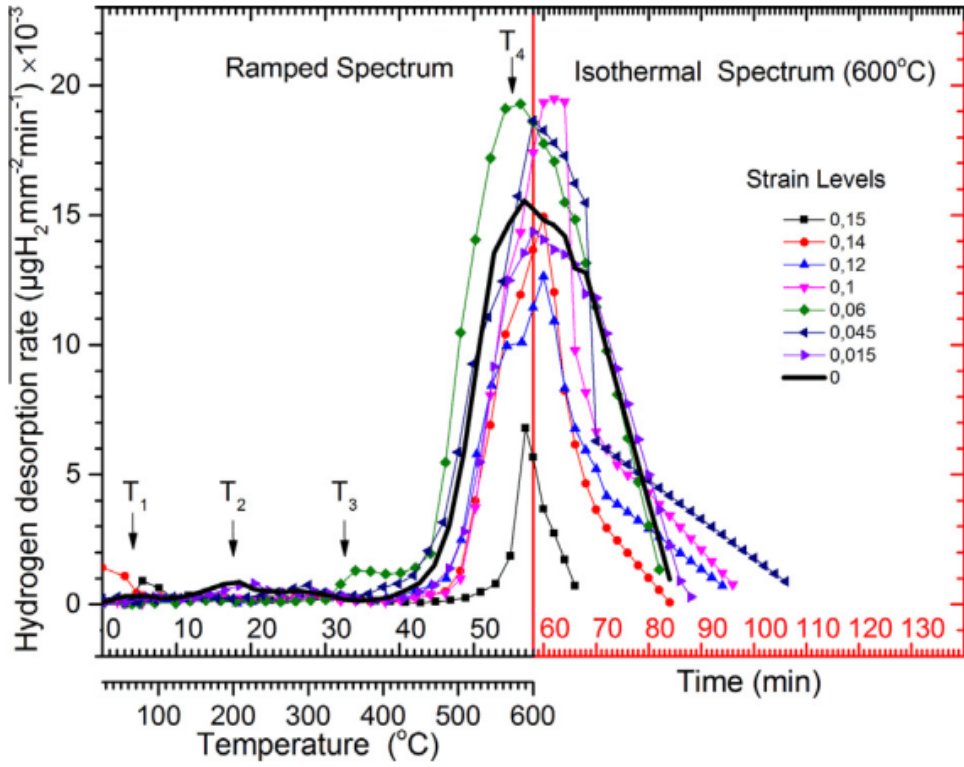


Figure 4-9: Diagram shows decrease in H trapped for strains above 0.06 for AA2024 [15]

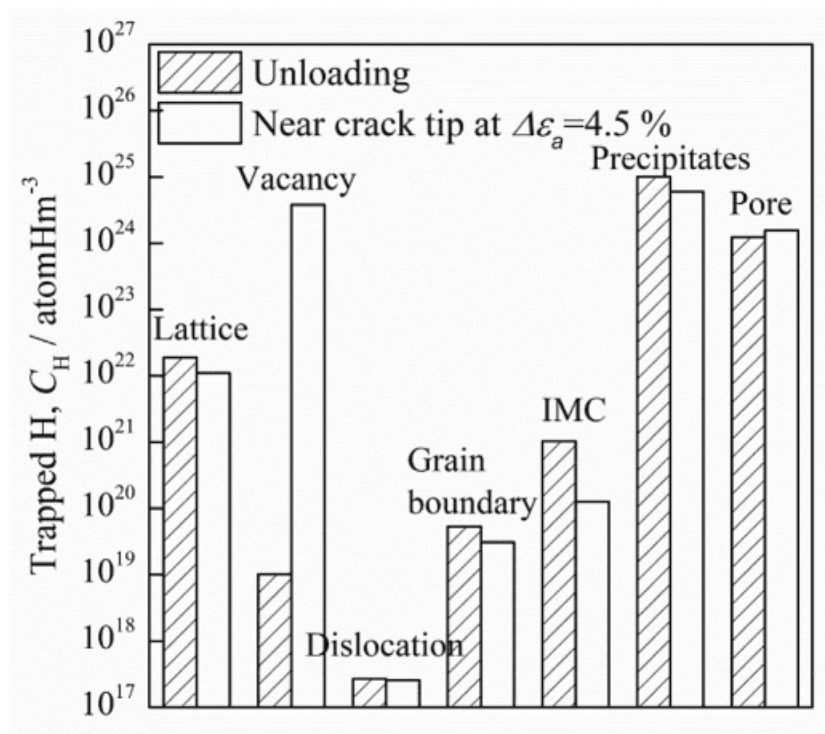


Figure 4-10: Trapped H content for precipitates for 4,5% strain conditions and unloading condition for 7xxx Al alloy [32]

Su et al. [32], on their study for 7xxx Al alloys present that decohesion of precipitates leads to 2,5 times more H trapped at precipitates and that increase in strain levels generate vacancy and dislocation emission, which help accumulate more hydrogen at several trap sites, with precipitates being one of them. At the same publication it is stated that hydrogen is trapped at angular corners due to hydrostatic tension concentration during deformation, something that remains the same for increase of strain levels. So, it is obvious that sites of strain concentration and decohesion of the matrix inside the alloy are sites prone to H trapping.

Lastly, Alexopoulos et al [36], mention the possibility that stretching during manufacturing may be responsible for precipitate formation.

4.9 Surface Treatment

There are no reports for interaction between surface treatment of precipitation hardening Al alloys and Hydrogen Embrittlement resistance, but there is a general approach analyzed by a study with examples mostly about steels [19] and a study with purpose of mitigating HE [34] that could be some guidelines. Surface coating is one possible solution, formation of a surface layer of different types like metallic, polymeric and ceramic [34], consisting of several elements, depending on the alloy [19] which protects the interior of the alloy. However, this layer is found to be destroyed in many cases due to deformations, strain and environment [19] and this destroy may lead to hydrogen liberation and absorption [34]. The other solution is surface modification, meaning surface nitriding, carbonizing and peening treatment, which are stated as promising ways to enhance HE resistance. For steels it is shown that they achieve high stability, compressive stress states, trapping of hydrogen near the surface and limitation of hydrogen diffusion inside the alloy [19].

One other mention regarding surface of a precipitation hardening Al alloy is found from Yamabe et al [47], which says for a 6061 alloy that intermetallic particles near the surface blocks the entry to the deep interior.

4.10 Environmental Conditions

Environmental conditions have to do with the atmosphere and temperature around a material, and for precipitation hardening Al alloys these conditions may affect the introduction and trapping of hydrogen and also the precipitates.

The presence of hydrogen around an alloy can be the result of exposure to corrosive environment, exposure to humid environment or cathodic charging [36]. A study for 2xxx Al alloys, using deuterium (D) as an equivalent for hydrogen, shows that the charging conditions influence the amount of D trapped and not the peak position of each trap and that for higher temperature charging conditions more D is trapped, as shown in Fig. 4-11 [23]. Moreover, 7xxx Al alloys charged with H during tensile tests in presence of both water vapor or argon atmosphere revealed that hydrogen amounts for the first situation were larger [18]. As shown in Fig. 4-12, hydrogen release at the wet environment is 10 times greater than the release at dry environment. Furthermore, cathodic reaction in corrosive environments produces hydrogen [23], and as anodic polarization progresses there is an increase of corrosion damage [58]. For a 2024 Al alloy, results reported that the alloy is more prone to corrosion if there is Cl⁻ in the solution during the service [58], thus more corroded product leads to more release of hydrogen.

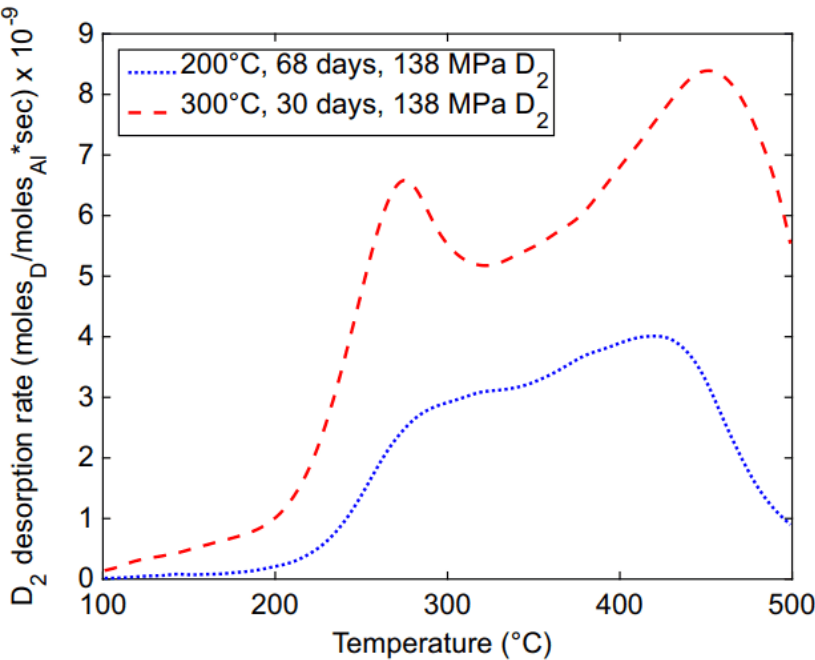


Figure 4-11: Diagram shows D amount for to different charging temperatures for 2xxx Al alloy [23]

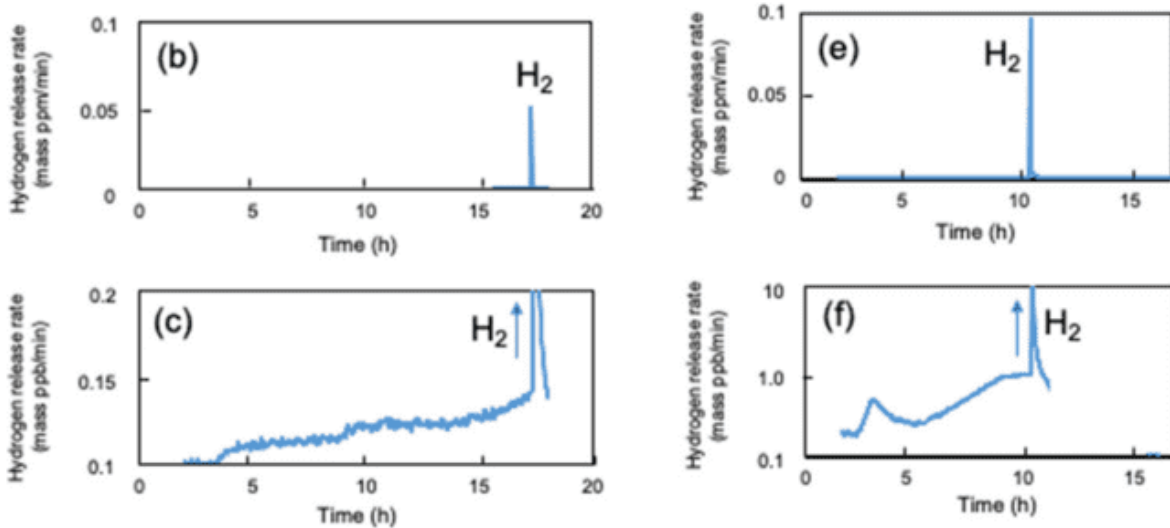


Figure 4-12: Hydrogen release for 7xxx Al alloy (left images) dry environment and (right images) wet environment. (c) and (f) are enlarged images of the vertical axes from (b) and (e) [18]

Moreover, for 2xxx precipitates there is a mention that high temperatures accessed during charging may cause coarsening or dissolution of precipitates [23], so it is generally useful to monitor and control the environmental temperature during in service time, in order not to have an unexpected change in the structure.

Simultaneously, exposure time of any alloy in their environment plays a significant role in the susceptibility for Hydrogen Embrittlement. For a 7046 Al alloy, amount of hydrogen seems to increase massively for the first exposure times at NaCl solution and then to almost stabilize for longer durations as shown in Fig. 4-13. However, for a 2024 Al alloy, Alexopoulos et al [36], reported that with exposure time to corrosion solution ductility always decreases, as shown in Fig. 4-14. Hence, there is no clear view on whether different exposure times alters the phenomenon of HE or not. A possible useful information comes also from Alexopoulos et al [36] because it is stated that shorter exposure times are selected to prevent surface pitting formation. The authors follow this process because they do not want to alter the embrittlement mechanism from being HE, but it is a potential strategy to not let pitting and localized corrosion and H accumulation to happen.

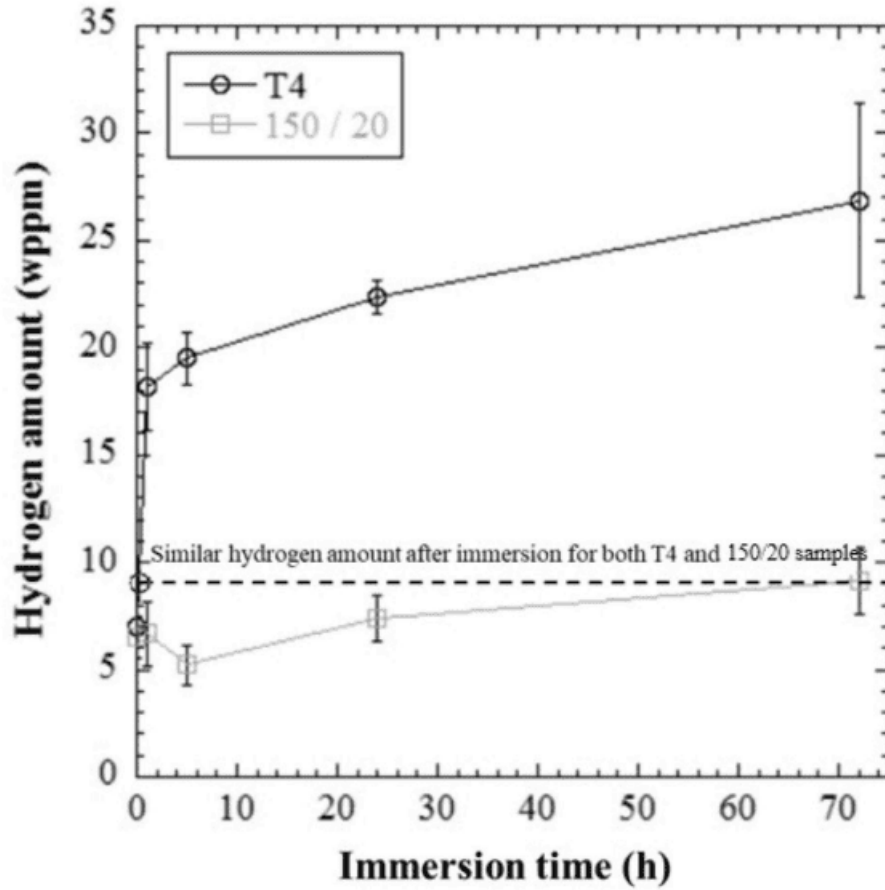


Figure 4-13: Hydrogen amount during exposure time at NaCl solution for AA7046 [28]

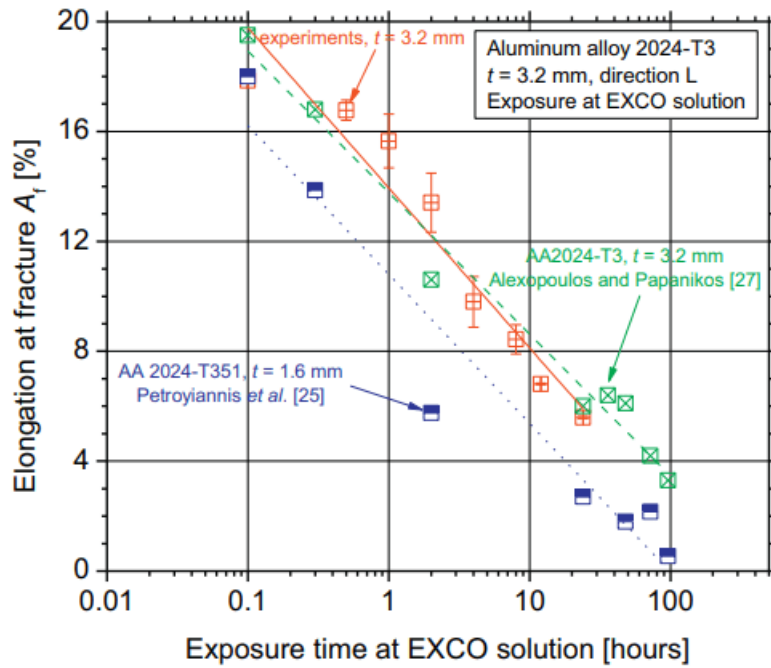


Figure 4-14: Ductility behavior during exposure time to corrosion solution for AA2024 [36]

Thus, regarding environment, high hydrogen or Cl^- content leads to more hydrogen trapping, while high temperatures may change the precipitation strengthening. Also, the first exposure times seems to trap hydrogen directly and after this, the duration of exposure is a controversial issue.

4.11 Corrosion

Corrosion is a main source of hydrogen for an alloy, so it causes H trapping [7,10] and simultaneously is a form of degradation for the alloy. Hydrogen is produced at a cathodic reaction during corrosion [7,36] and it is shown that hydrogen uptake from the precipitation hardening alloys (studies for 7xxx) can increase susceptibility to Hydrogen Embrittlement and after a critical amount it can lead to Hydrogen Induced Cracking (HIC) [7,35]. Experiments for 2024 Al alloys [10,36] reported that when precipitates become more established, during the evolution of ageing, corrosion increases and these intermetallic particles may change corrosion from general to localized. Thus, precipitation phases not only may trap H after corrosion, but they afflict corrosion damage. Lastly, study for 2024 alloy resulted in corrosion depth $350\mu\text{m}$ for the specimens, as shown in Fig. 4-15, and penetration of H was estimated around $400\mu\text{m}$ and $500\mu\text{m}$ [29]. So, it occurs that corrosion influence more fraction of the material than just the exposed surface. This observation is consistent with the fact that removal of corrosion layer leads to partial restoration of ductility [29], hence it is not an affective protection against HE for the material.

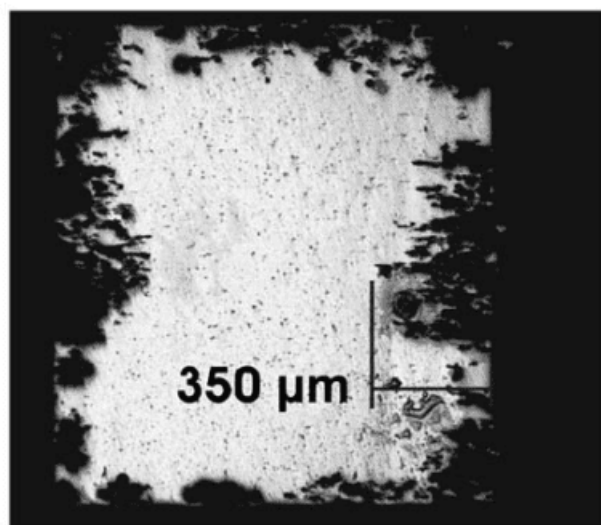


Figure 4-15: Determination of corrosion layer depth for AA2024 [29]

Chapter 5. Beneficial effects of precipitates

Previous research about the phenomenon of Hydrogen Embrittlement talks about some beneficial effects that precipitates may have, apart from the concerning influence of them during the hydrogen trapping. Precipitates inside an Al alloy are irreversible traps for hydrogen, and the partition of hydrogen into these particles inhibits the amount of solute H in the matrix [5,7,34]. Their strong binding energies, as shown in Fig. 5-1, are evidence of their ability to attract hydrogen from the matrix. Studies concerning 7xxx Al alloys (7068,7046), mention semi-coherent precipitates with a discontinuous distribution that constitute interrupted paths for hydrogen and decrease the H diffusion rate [6,13,28], delaying a possible premature fracture. Also, other equivalent studies (7046,7180,7A99) mention coarse and incoherent precipitates that act as barrier and lower the amount of hydrogen that reaches grain boundaries [7,13,59,60], which are energetically favored trapping sites for 7xxx Al alloys, as mentioned in chapter 2. Moreover, for coarse precipitates it is reported that the larger inter-precipitate distance can lead to formation of molecular hydrogen minimizing the presence of atomic hydrogen [6] that may accumulate at the microstructure. It is mentioned that these interactions can improve Hydrogen Embrittlement, Hydrogen Induced Cracking resistance, brittle fracture, corrosion resistance or Stress Corrosion Cracking.

Precipitate type	Matrix structure	H binding energy E_b (kJ/mol)
Steels		
TiC	α	28.1–94.5
Fe ₃ C	α	8.4–83.9
VC	α	24.8–59.6
NbC	α	77.2
NbN	α	100–143 ^a
Mo ₂ C	α	22–28
Al alloys		
η -MgZn ₂	γ	28.8–38.4
Al ₂ CuMg	γ	36.0
Al ₂ Cu	γ	19.3–40.3
Al ₃ Li	γ	25.2
Al ₂ CuLi	γ	38

Figure 5-1: Binding energies of different precipitate types. η -MgZn₂, θ -Al₂CuMg and θ -Al₂Cu precipitates are more important for precipitation hardening [34]

However, the beneficial effects of precipitates are not certain, and the parameters of effectiveness at a potential mitigation strategy using precipitates are the same as mentioned above about HE susceptibility. The characteristics of second-phase particles, such as chemistry, size and morphology, the matrix, the dispersoids and the service or testing environment play a significant role [5,34]. Sun et al [34], during their studying of microstructure design strategies to lower Hydrogen Embrittlement reveal that precipitates and the related interfaces between matrix and precipitates must be immune to hydrogen induced damage and the precipitates must not become saturated throughout the service or the experiment in order to have beneficial effects against HE. Thus, precipitates are recognized as useful if they have structures that can tolerate hydrogen damage and if they are surrounded by an environment with controlled hydrogen ingress. For precipitation hardening Al alloys there is no full research, to the author knowledge, regarding immunity of their precipitates against hydrogen. Also, many applications which use precipitation hardening Al alloys for hydrogen storage or transport cannot rely on precipitates to enhance HE resistance because there is abundant hydrogen.

Chapter 6. Conclusions

Hydrogen trapping for precipitation hardening Al-alloys happens at many microstructural features, but an energetically favored and important trapping site is the precipitates, which are essential for the strengthening of the Al alloys. Ingress from environment and adsorption of hydrogen at precipitates and other features and defects that interact with precipitates in combination with the conditions around of the material lead to Hydrogen Embrittlement of the alloy. Studying of all the above issues is important, so the present work resulted in the following conclusions:

- The strongest hydrogen trapping sites for precipitation hardening Al alloys are precipitates, vacancies, grain boundaries or pores.
- There is a high trapping capacity for incoherent precipitates, a medium for semi-coherent and a weak for coherent precipitates.
- Hydrogen at coherent precipitates leads to pitting and hydrogen at incoherent precipitates forms micro-cracks.
- Chemistry of the precipitates does not seem to affect hydrogen trapping, in general.
- Nucleation and growth of S phase may constrain θ phase nucleation.
- Intragranular precipitates between 4.6 ± 1 nm and 10.6 ± 1 nm trap more hydrogen and intergranular precipitates between 23 ± 2 nm and 36 nm may trap more hydrogen.
- For 2xxx Al alloys, precipitates with thicknesses from around 3 nm to around 8 nm show a better resistance to HE.
- Hydrogen trapping power for precipitates after coarsening is generally low.
- Granular precipitates may trap more hydrogen than plate-like, plate-like precipitates may trap more hydrogen than rod-like and lath-like precipitates may trap more hydrogen than needle-like. Also, equilibrium round S precipitates trap hydrogen.
- Semi-coherent and incoherent precipitates increase the density of dislocations, and dislocations may be trapping sites or may be short-circuiting diffusion paths for hydrogen.

- Grain boundary precipitates are created at grain boundaries and are coarser than matrix precipitates, around 20-50 nm.
- Grain boundary precipitates may lead to formation of molecular hydrogen instead of atomic.
- Grain boundaries are a weak trapping site for hydrogen, but they are short-circuiting diffusion paths.
- Grain boundaries have higher binding energy with hydrogen than lath boundaries.
- Vacancies are energetically favored trapping sites for 7xxx alloys and they are involved in a Hydrogen Embrittlement mechanism.
- Dispersoids can be created for precipitation hardening alloys and they concentrate precipitates and hydrogen around them.
- Increasing of Cu content increases amount of trapped hydrogen and the peak area for precipitates trap.
- Mn and Zr atoms may create dispersoids for 2xxx and 7xxx Al alloys respectively.
- For 7xxx Al alloys, Mn additions may enhance HE resistance.
- Mg increase solubility of hydrogen and has high binding energy with hydrogen leading to co-segregation and H-induced cracking.
- Presence of Fe and Si decreases fracture strain and absence of them decreases micropores.
- Presence of hydrogen at the crack tips provokes dislocations and vacancies emission and multiplication and dislocations movement.
- Plastic deformation prior to corrosion or increase in applied strain levels are reported to cause decrease of hydrogen diffusivity and hydrogen content at precipitates.
- Sites of strain concentration and decohesion of the matrix inside the alloy are sites prone to hydrogen trapping.
- Precipitates can trap hydrogen limiting the atomic hydrogen at the microstructure, decrease hydrogen diffusion rate towards dangerous trapping sites and have a beneficial effect on Hydrogen Embrittlement.

- Precipitates can be beneficial if they are immune to H-induced damage and if they do not become saturated.

Based on all the research and analysis of the issue some guidelines for designing hydrogen tolerant precipitation hardening Al alloys are:

- Precipitates should try maintaining their coherency with the matrix, of course in combination with maintaining the desirable strength level.
- Precipitates inside the grains should have sizes smaller than 4.6 ± 1 nm or larger than 10.6 ± 1 nm, and precipitates at the grain boundaries should have sizes smaller than 23 ± 2 nm or larger than 36 nm, in the amount that it does not downgrade the alloys' properties. Besides, precipitates should be coarse, but within a limit in order not to minimize the strength.
- For 2xxx alloys, precipitates should have thicknesses around 3 nm and 8 nm to achieve less ductility decrease.
- Precipitates should be needle-like or rod-like in order to trap less hydrogen. Formation of granular and round precipitates should be avoided.
- Dislocations should remain in a low density and the existing dislocations should be monitored. Dislocations are a medium-energy sites thus not dangerous, so more hydrogen trapped at them leads to general decrease at the atomic hydrogen.
- Grain boundaries should be preferential sites for precipitates nucleation because these precipitates are coarser and coarser precipitates, as mentioned above trap less hydrogen. Also, the bigger inter-precipitate distance between grain boundary precipitates may lead to formation of molecular hydrogen.
- Annealing out of frozen-in vacancies is beneficial, especially for 7xxx alloys, so during heat treatment, exposure time should be long enough for annealing out to happen, if it is possible.
- Cu content should be as low as possible, without limiting the desirable amount of θ phase.
- For 7xxx alloys, Zr content should be as low as possible.
- For 2xxx alloys, Mn content should be as low as possible.
- For 7xxx alloys, Mn is a desirable element because it can help HE resistance.

- Mg content should be as low as possible, without limiting the desirable amount of β , η or S phases.
- Fe and Si content should be zero or as low as possible.
- Zn content do not affect hydrogen trapping, so there is no limitation for Zn atoms.
- Temperature during heat treatment should be at an intermediate level, not very high in order not to dissolve already formed precipitates and not very low in order not to lead to a well-distributed formation of precipitates that ends up in many trapping sites.
- Heating of the alloy periodically, if it is possible, can liberate trapped hydrogen.
- Deformations prior to or during alloy's exposure to hydrogen may be helpful, due to decrease of hydrogen diffusivity and trapping.
- Surface modification (nitriding, carbonizing or peening treatment) promotes resistance to HE for steels and may help Al alloys as well.
- Surface coating is found to be a dangerous approach for alloys, so it is not recommended.
- Generation, manufacturing and operation of the Al alloy at dry, non-corrosive and non-hydrogen rich environment, without Cl^- and absence of very high temperature is safer for the alloy.
- Control at the amount of accumulated hydrogen, in order to have knowledge of the level of saturation at the trapping sites is useful.

The above guidelines are general suggestions based on results, mostly for specific precipitation hardening Al alloys, that appear in many cases. Due to repeated identical or similar results a general approach occurs. However, apart from this, all the particular examples and observations that are analyzed in the present work may be helpful depending on the specific situation or applications.

Based on these guidelines and all the information about precipitation hardening Al alloys Thermo-Calc software package is a useful tool for designing of an alloy. The main Thermo-Calc (thermodynamical) mode, the diffusion module (Prisma) and mostly the precipitation module (Prisma) can be used to perform calculations and simulations. The user

can select the phases to be present for the calculations, the elements of the alloy, the compositions of the elements, the environmental temperature during the precipitation and the dislocations density for some calculations. Also, Thermo-Calc can calculate all the stable and metastable phases that exist inside an alloy, the volume fraction of each phase and the mass fraction of each element for a specific phase. Moreover, Prisma can simulate multiple equilibrium and metastable conditions during precipitation, put them in the same simulation and compare them and it can calculate the existing phases (including precipitation phases) at a specific temperature. The user of Prisma can alter the nucleation sites for precipitation and select precipitation at the bulk, at grain boundaries or at dislocations. The simulations can show results for the radius and the size of precipitates and for the distribution of them at a function of time. In addition, Dictra may be useful for a simulation of hydrogen diffusion inside an Al alloy. As a result, the chemistry and the size of precipitates, the dislocations, the alloying elements and the grain boundaries, the H diffusion and also the temperature and the ageing time can be studied through these simulation tools.

References

- [1]. Guillaume Hachet, Xavier Sauvage, (2022) Hydrogen delaying the formation of Guinier-Preston zones in aluminium alloys. *Acta Materialia*, 241, 118373
- [2]. Masashi Inoue, Teppei Otsuka, Keitaro Imae, Alihide Azuma, (2021) Retention characteristics of hydrogen in pure aluminum and duralumin with cold-working. *Fusion Engineering and Design*, 170, 112711
- [3]. IAN M. ROBERTSON, P. SOFRONIS, A. NAGAO, M.L. MARTIN, S. WANG, D.W. GROSS, K.E. NYGREN, (2015) Hydrogen Embrittlement Understood. *The Minerals, Metals & Materials Society and ASM International*, 46B, 1085-1103
- [4]. TOMOHITO TSURU, KATSUHIKO NISHIMURA, KENJI MATSUDA, NOIRO NUNOMURA, TAKAHIRO NAMIKI, SEUNGWON LEE, WATARU HIGEMOTO, TEIICHIRO MATSUZAKI, MASATAKE YAMAGUCHI, KENICHI EBIHARA, KAZUYUKI SHIMIZU, HIROYUKI TODA, (2023) Identification of Hydrogen Trapping in Aluminum Alloys Via Muon Spin Relaxation Method and First-Principles Calculations. *METALLURGICAL AND MATERIALS TRANSACTIONS A*, 54, 2374-2383
- [5]. Huan Zhao, Poulami Chakraborty, Dirk Ponge, Tilmann Hickel, Binhan Sun, Chun-Hung Wu, Baptiste Gault, Dierk Raabe, (2022) Hydrogen trapping and embrittlement in high-strength Al alloys. *Nature*, 602, 437-441
- [6]. Ankur Kumar, Gajanan P. Chaudhari, S.K. Nath, (2022) Correlation of microstructure with corrosion performance in high zinc 7068 aluminum alloy aged using different T6 conditions. *Materials Characterization* 191, 112133
- [7]. Yuzhu Hou, Liang Chen, Zhigang Li, Guoqun Zhao, Cunsheng Zhang, (2020) Effects of artificial aging on microstructure, mechanical properties and stress corrosion cracking of a novel high strength 7A99 Al alloy. *Materials Science & Engineering A*, 780, 139217
- [8]. Fan Zhang, Lyle E. Levine, Andrew J. Allen, Carelyn E. Campbell, Adam A. Creuziger, Nataliya Kazantseva, Jan Ilavsky, (2016) In situ structural characterization of ageing kinetics in aluminum alloy 2024 across angstrom-to-micrometer length scales. *Acta Materialia*, 111, 385-398

- [9]. Yong Zhang, Colleen Bettles, Paul A. Rometsch, (2014) Effect of recrystallisation on Al₃Zr dispersoid behaviour in thick plates of aluminium alloy AA7150. *Journal of Material Science*, 49, 1790-1715
- [10]. H. Kamoutsi, G.N. Haidemenopoulos, H. Mavros, C. Karantonidis, P. Floratos, Z. Alhosani, P. Cho, D.H. Anjum, F. Ravaux, K. Polychronopoulou, (2021) Effect of precipitate coherency on the corrosion-induced hydrogen trapping in 2024 aluminum alloy. *International journal of hydrogen energy*, 46, 34487-34497
- [11]. Mahdieh Safyari, Masoud Moshtaghi, Shigeru Kuramoto, (2021) On the role of traps in the microstructural control of environmental hydrogen embrittlement of a 7xxx series aluminum alloy. *Journal of Alloys and Compounds*, 855, 157300
- [12]. A. Lervik, C.D. Marioara, M. Kadanik, J.C. Walmsley, B. Milkereit, R. Holmestad, (2020) Precipitation in an extruded AA7003 aluminium alloy: Observations of 6xxx-type hardening phases. *Materials and Design*, 186, 108204
- [13]. Loïc Oger, Manon Chloé Lafouresse, Grégory Odemer, Lionel Peguet, Christine Blanc, (2017) Hydrogen diffusion and trapping in a low copper 7xxx aluminium alloy investigated by Scanning Kelvin Probe Force Microscopy. *Materials Science & Engineering A*, 706, 126–135
- [14]. Md. Shahnewaz Bhuiyan, Hiroyuki Toda, Zhang Peng, Su Hang, Keitaro Horikawa, Kentaro Uesugi, Akihisa Takeuchi, Nobuto Sakaguchi, Yoshio Watanabe, (2016) Combined microtomography, thermal desorption spectroscopy, X-ray diffraction study of hydrogen trapping behavior in 7XXX aluminum alloys. *Materials Science & Engineering A*, 655, 221–228
- [15]. H. Kamoutsi, G.N. Haidemenopoulos, V. Bontozoglou, P.V. Petroyiannis, Sp.G. Pantelakis, (2014) Effect of prior deformation and heat treatment on the corrosion-induced hydrogen trapping in aluminium alloy 2024. *Corrosion Science*, 80, 139–142
- [16]. T. Tsuru, M. Yamaguchi, K. Ebihara, M. Itakura, Y. Shiihara, K. Matsuda, H. Toda, (2018) First-principles study of hydrogen segregation at the MgZn₂ precipitate in Al-Mg-Zn alloys. *Computational Materials Science*, 148, 301-306
- [17]. Hang Su, Hiroyuki Toda, Ryohei Masunaga, Kazuyuki Shimizu, Hongye Gao, Katsuro Sasaki, Md Shahnewaz Bhuiyan, Kentaro Uesugi, Akihisa Takeuchi, Yoshio Watanabe, (2018) Influence of hydrogen on strain localization and fracture behavior in Al₂ZnMgCu aluminum alloys. *Acta Materialia*, 159, 332-343

- [18]. Keitaro Horikawa, (2021) Quantitative monitoring of the environmental hydrogen embrittlement of Al-Zn-Mg-based aluminum alloys via dynamic hydrogen detection and digital image correlation. *Scripta Materialia*, 199, 113853
- [19]. Xinfeng Li, Xianfeng Ma, Jin Zhang, Eiji Akiyama, Yanfei Wang, Xiaolong Song, (2020) Review of Hydrogen Embrittlement in Metals: Hydrogen Diffusion, Hydrogen Characterization, Hydrogen Embrittlement Mechanism and Prevention. *Acta Metallurgica Sinica (English Letters)*, 33, 759–773
- [20]. Ujwal Shreenag Meda, Nidhi Bhat, Aditi Pandey, K.N. Subramanya, M.A. Lourdu Antony Raj, (2023) Challenges associated with hydrogen storage systems due to the hydrogen embrittlement of high strength steels. *international journal of hydrogen energy*, 48, 17894-17913
- [21]. N. Takano, (2008) Hydrogen diffusion and embrittlement in 7075 aluminum alloy. *Materials Science and Engineering A*, 483–484, 336–33
- [22]. E. Pouillier, A.-F. Gourgues, D. Tanguy, E.P. Busso, (2012) A study of intergranular fracture in an aluminium alloy due to hydrogen embrittlement. *International Journal of Plasticity*, 34, 139–153
- [23]. Paul Chao, Richard A. Karnesky, (2016) Hydrogen isotope trapping in Al–Cu binary alloys. *Materials Science & Engineering A*, 658, 422–428
- [24]. Reza Parvizi, Ross K. W. Marceau, Anthony E. Hughes, Mike Y. Tan, Maria Forsyth, (2014) Atom Probe Tomography Study of the Nanoscale Heterostructure around an Al₂₀Mn₃Cu₂ Dispersoid in Aluminum Alloy 2024. *Langmuir*, 30, 14817-14823
- [25]. Jiding Zhang, Yue Sheng, Hongda Yang, Wentao Ma, Xiaoyu Jiang, (2023) Crystal crack dislocation model and micro-crack nucleation criterion in the hydrogen environment. *European Journal of Mechanics / A Solids*, 98, 104899
- [26]. Γρηγόρης Ν. Χαϊδεμενόπουλος, Ισχυροποίηση με καθίζηση, *Φυσική Μεταλλουργία*, Εκδόσεις Τζιόλα, Θεσσαλονίκη, 499-207, 2017
- [27]. Yuanyuan Li, Qian Wang, Huawei Zhang, Hongyi Zhu, Mingliang Wang, Haowei Wang, (2023) Role of solute atoms and vacancy in hydrogen embrittlement mechanism of aluminum: A first-principles study. *international journal of hydrogen energy*, 48, 4516-4528

- [28]. L. Oger, E. Andrieu, G. Odemer, L. Peguet, C. Blanc, (2020) Hydrogen - dislocation interactions in a low-copper 7xxx aluminium alloy: About the analysis of interrupted stress corrosion cracking tests. *Materials Science & Engineering A*, 790, 139654
- [29]. H. Kamoutsi, G.N. Haidemenopoulos, V. Bontozoglou, S. Pantelakis, (2006) Corrosion-induced hydrogen embrittlement in aluminum alloy 2024. *Corrosion Science*, 48, 1209–1224
- [30]. A. Turnbull, Hydrogen diffusion and trapping in metals, *Gaseous Hydrogen Embrittlement of Materials in Energy Technologies*, Richard P. Gangloff, Brian P. Somerday, Woodhead Publishing Series in Metals and Surface Engineering, 89-128, 2012
- [31]. Qinglong Liu, Jeffrey Venezuela, Mingxing Zhang, Qingjun Zhou, Andrej Atrens, (2016) Hydrogen trapping in some advanced high strength steels. *Corrosion Science*, 111, 770-785
- [32]. Hang Su, Hiroyuki Toda, Kazuyuki Shimizu, Kentaro Uesugi, Akihisa Takeuchi, Yoshio Watanabe, (2019) Assessment of hydrogen embrittlement via image-based techniques in AlZnMgCu aluminum alloys. *Acta Materialia*, 176, 96-108
- [33]. E. Charitidou, G. Papapolymerou, G.N. Haidemenopoulos, N. Hasiotis, V. Bontozoglou, (1999) CHARACTERIZATION OF TRAPPED HYDROGEN IN EXFOLIATION CORRODED ALUMINIUM ALLOY 2024. *Scripta Materialia*, 41 (12), 1327-1332
- [34]. Binhan Sun, Xizhen Dong, Jianfeng Wen, Xian-Cheng Zhang, Shan-Tung Tu, (2023) Microstructure design strategies to mitigate hydrogen embrittlement in metallic materials. *Fatigue & Fracture of Engineering Materials & Structures*, 46 (8), 2721-3117
- [35]. Mahdieh Safyari, Gregor Mori, Stephan Ucsnik, Masoud Moshtaghi, (2023) Mechanisms of hydrogen absorption, trapping and release during galvanostatic anodization of high-strength aluminum alloys. *Journal of Materials Research and Technology*, 22, 80-88
- [36]. Nikolaos D. Alexopoulos, Zaneta Velonaki, Constantinos I. Stergiou, Stavros K. Kourkoulis, (2016) The effect of artificial ageing heat treatments on the corrosion-induced hydrogen embrittlement of 2024 (Al–Cu) aluminium alloy. *Corrosion Science*, 102, 413-424

- [37]. H. SAITOH, Y. IJIMA, K. HIRANO, (1994) Behaviour of hydrogen in pure aluminium, Al-4 mass % Cu and Al-1 mass% Mg₂Si alloys studied by tritium electron microautoradiography. *Journal of Materials and Science*, 29, 5739-5744
- [38]. Andrew C. Lee, Abhinav Parakh, Andrew Sleugh, Ottman A. Tertuliano, Sebastian Lam, Johanna Nelson Weker, Peter Hosemann, X. Wendy Gu, (2023) Detection of voids in hydrogen embrittled iron using transmission X-ray microscopy. *International Journal of Hydrogen Energy*, 48, 1968-1978
- [39]. Sandeep Kumar Dwivedi, Manish Vishwakarma, (2018) Hydrogen embrittlement in different materials: A review. *International Journal of Hydrogen Energy*, 43, 21603-21616
- [40]. Shuang Liang, Minsheng Huang, Lv Zhao, Yaxin Zhu, Zhenhuan Li, (2021) Effect of multiple hydrogen embrittlement mechanisms on crack propagation behavior of FCC metals: Competition vs. synergy. *International Journal of Plasticity*, 143, 103023
- [41]. Milos B. Djukic, Gordana M. Bakic, Vera Sijacki Zeravcic, Aleksandar Sedmak, Bratislav Rajcic, (2019) The synergistic action and interplay of hydrogen embrittlement mechanisms in steels and iron: Localized plasticity and decohesion. *Engineering Fracture Mechanics*, 216, 106528
- [42]. Marina Yu. Panchenko, Galina G. Maier, Irina A. Tumbusova, Sergey V. Astafurov, Eugene V. Melnikov, Valentina A. Moskvina, Alexander G. Burlachenko, Yurii A. Mirovoy, Yurii P. Mironov, Nina K. Galchenko, Elena G. Astafurova, (2019) The effect of age-hardening mechanism on hydrogen embrittlement in high-nitrogen steels. *International Journal of Hydrogen Energy*, 44, 20529-20544
- [43]. Yuhei Ogawa, Kohei Noguchi, Osamu Takakuwa, (2022) Criteria for hydrogen-assisted crack initiation in Ni-based superalloy 718. *Acta Materialia*, 229, 117789
- [44]. Yang He, Yaojun Li, Xiong Zhao, Haobo Yu, Changfeng Chen, (2019) Effect of hydrogen atom and hydrogen filled vacancies on stacking fault energy in α -Fe by first principles calculations. *International Journal of Hydrogen Energy*, 44, 17136-17145
- [45]. R. Kirchhei, A. Pundt, (2014) Hydrogen in Metals. *Physical Metallurgy (Fifth Edition)*, 2597-2705
- [46]. W. Li, X. Zhu, C. Wang, X. Jin, (2015) Effect of S-phase on the hydrogen induced phase transition and hydrogen embrittlement susceptibility in AISI 304 stainless steel. *Materials Today: Proceedings 2S*, S691 – S695

- [47]. Junichiro Yamabe, Tohru Awane, Yukitaka Murakami, (2017) Hydrogen trapped at intermetallic particles in aluminum alloy 6061-T6 exposed to high-pressure hydrogen gas and the reason for high resistance against hydrogen embrittlement. *International Journal of Hydrogen Energy*, 42, 24560-24568
- [48]. Masoud Moshtaghi, Mahdiah Safyari, Shigeru Kuramoto, Tomohiko Hojo, (2021) Unraveling the effect of dislocations and deformation-induced boundaries on environmental hydrogen embrittlement behavior of a cold-rolled AlZnMgCu alloy. *International Journal of Hydrogen Energy*, 46, 8285-8299
- [49]. G. A. YOUNG JR, J. R. SCULLY, (1998) THE DIFFUSION AND TRAPPING OF HYDROGEN IN HIGH PURITY ALUMINUM. *Acta Materialia*, 46, 6337-6349
- [50]. YOSHIAKI IJIMA, SHIN-ICHI YOSHIDA, HIDEYUKI SAITOH, HIROSHI TANAKA, KEN-ICHI HIRANO, (1992) Hydrogen trapping and repelling in an Al-6 wt % Zn-2 wt % Mg alloy. *Journal of Materials Science*, 27, 5735-5738
- [51]. J.K. Sunde, C.D. Marioara, A.T.J. van Helvoort, R. Holmestad, (2018) The evolution of precipitate crystal structures in an Al-Mg-Si(-Cu) alloy studied by a combined HAADF-STEM and SPED approach. *Materials Characterization*, 142, 458-469
- [52]. Shweta Shukla, Balila Nagamani Jaya, V.S. Raja, (2023) Micro-mechanisms of deformation accommodation in AA7050 alloy in the presence of hydrogen. *Journal of Alloys and Compounds*, 947, 169596
- [53]. R.G. Song, W. Dietzel, B.J. Zhang, W.J. Liu, M.K. Tseng, A. Atrens, (2004) Stress corrosion cracking and hydrogen embrittlement of an Al-Zn-Mg-Cu alloy. *Acta Materialia*, 52, 4727-4743
- [54]. Mingyang Chen, Shengdan Liu, Kezhun He, Xu Zheng, Yong Zhang, Jianguo Tang, Lingying Ye, (2023) Hydrogen-induced failure in a partially-recrystallized Al-Zn-Mg-Cu alloy with different aging conditions: Influence of deformation behavior dominated by microstructures. *Materials & Design*, 233, 112199
- [55]. Aniruddha Biswas, Donald J. Siegel, C. Wolverton, David N. Seidman, (2011) Precipitates in Al-Cu alloys revisited: Atom-probe tomographic experiments and first-principles calculations of compositional evolution and interfacial segregation. *Acta Materialia*, 59, 6187-6204

- [56]. S. C. Wang, M. J. Starink, (2005) Precipitates and intermetallic phases in precipitation hardening Al–Cu–Mg–(Li) based alloys. *International Materials Reviews*, 50 (4), 193-215
- [57]. Yuantao Xu, Hiroyuki Toda, Kazuyuki Shimizu, Yafei Wang, Baptiste Gault, Wei Li, Kyosuke Hirayama, Hiro Fujihara, Xuejun Jin, Akihisa Takeuchi, Masayuki Uesugi, (2022) Suppressed hydrogen embrittlement of high-strength Al alloys by Mn-rich intermetallic compound particles. *Acta Materialia*, 236, 118110
- [58]. Hong Ju, Shufa Liu, Wei Zhang, Yuanfeng Yang, Jinzhuo Duan, (2021) Investigation of pitting corrosion and hydrogen evolution of aluminum and AA2024 alloy by simultaneous electrochemical measurements and imaging. *Electrochemistry Communications*, 132, 107135
- [59]. N. Ben Ali, D. Tanguy, R. Estevez, (2011) Effects of microstructure on hydrogen-induced cracking in aluminum alloys. *Scripta Materialia*, 65, 210–213
- [60]. L. Stermann, G. Simon, L. Vanel, D. Tanguy, (2023) In situ measurement of plasticity accompanying hydrogen induced cracking in a polycrystalline AlZnMg alloy. *International Journal of Hydrogen Energy*, 48 (73), 28567-28582