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DEPARTMENT OF MECHANICAL ENGINEERING

High-strength aluminum alloys for high-pressure hydrogen storage



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Submitted to the Department of Mechanical Engineering on February 2023 in partial fulfillment of requirements for the degree of Master

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Abstract

Transportation significantly contributes to global energy consumption, mainly due to internal combustion engines. The dependence on fossil fuels, which are non-renewable and polluting, has resulted in an energy and environmental crisis. As a result, researchers are exploring renewable alternatives to decrease this dependency. Hydrogen is a promising choice as it boasts high energy density, efficiency, and produces zero greenhouse gas emissions when utilized as fuel. However, there are technical obstacles to the widespread adoption of hydrogen, such as the absence of secure, lightweight, and energy-efficient ways to store it on board vehicles.

Hydrogen is typically stored in compressed tanks. This method is the most widely used method to store hydrogen. Cryogenic and cry-compressed tanks are also different ways to store hydrogen. Also, chemical storage is used for hydrogen. This project focuses on the compressed hydrogen tanks and the materials that are used to construct them.

For compressed hydrogen storage there are several properties that are required for the tank's material: high storage density, safety, durability, low weight, corrosion resistance and to be easily to transport. Also, for the construction of a vessel should be taken into account the external and internal pressure. Aluminum is a material that meets these requirements due to its various beneficial properties and it is suitable for use in hydrogen storage tanks. Specifically, the Al-Cu alloys-2xxx, the Al-Mg alloys-5xxx, the Al-Mg-Si alloys-6xxx, the Al-Zn alloys-7xxx and Al-Li alloys include materials that are used in hydrogen storage tanks because of their properties.

Although high-strength aluminum alloys have desirable properties for hydrogen tanks, they suffer from hydrogen embrittlement when in touch with hydrogen, resulting in decreased mechanical properties and a risk of cracking before the expected point. Hydrogen embrittlement arises from the diffusion and trapping of hydrogen atoms, which promotes stress corrosion cracking. Various models have been proposed to explain this phenomenon, and there are techniques available to test the materials and prevent hydrogen embrittlement. Apart from these preventative measures, alternative materials like Magnesium and Titanium-based alloys show promise as a solution.

Περίληψη

Οι μεταφορές συμβάλλουν σημαντικά στην παγκόσμια κατανάλωση ενέργειας και την ενεργειακή κρίση, κυρίως λόγω των κινητήρων εσωτερικής καύσης. Η εξάρτηση από τα ορυκτά καύσιμα, τα οποία είναι μη ανανεώσιμα και ρυπογόνα, έχει οδηγήσει σε ενεργειακή και περιβαλλοντική κρίση. Ως αποτέλεσμα, γίνονται προσπάθειες ώστε να βρεθούν εναλλακτικές λύσεις από ανανεώσιμες πηγές για να μειώσουν αυτή την εξάρτηση. Το υδρογόνο είναι μια πολλά υποσχόμενη επιλογή, καθώς διαθέτει υψηλή ενεργειακή πυκνότητα, απόδοση και μηδενικές εκπομπές αερίων θερμοκηπίου όταν χρησιμοποιείται ως καύσιμο. Ωστόσο, υπάρχουν τεχνικά εμπόδια στην ευρεία χρήση του υδρογόνου ως καύσιμο, όπως θέματα ασφαλείας, ύπαρξη ελαφριών και ενεργειακά αποδοτικών κατασκευών για την αποθήκευση του υδρογόνου.

Το υδρογόνο συνήθως αποθηκεύεται σε συμπιεσμένη μορφή. Αυτή η μέθοδος είναι η πιο ευρέως χρησιμοποιούμενη μέθοδος αποθήκευσης υδρογόνου. Οι κρυογονικές (cryogenic) και οι συμπιεσμένες κρυογονικές (cryo-compressed) δεξαμενές είναι επίσης διαφορετικοί τρόποι αποθήκευσης υδρογόνου. Επίσης, για την αποθήκευση του υδρογόνου χρησιμοποιείται και χημική αποθήκευση. Η συγκεκριμένη εργασία εστιάζει στις δεξαμενές συμπιεσμένου υδρογόνου και στα υλικά που χρησιμοποιούνται για την κατασκευή τους.

Για την αποθήκευση συμπιεσμένου υδρογόνου απαιτούνται διάφορες ιδιότητες για το υλικό της δεξαμενής: υψηλή πυκνότητα αποθήκευσης, ασφάλεια, ανθεκτικότητα, χαμηλό βάρος, αντοχή στη διάβρωση και εύκολη μεταφορά. Επίσης, για την κατασκευή της δεξαμενής θα πρέπει να λαμβάνεται υπόψη η εξωτερική και εσωτερική πίεση, συνθήκες λειτουργίας. Το αλουμίνιο είναι ένα υλικό που πληροί αυτές τις απαιτήσεις λόγω των διαφόρων επιθυμητών ιδιοτήτων του και είναι κατάλληλο για χρήση σε δεξαμενές αποθήκευσης υδρογόνου. Συγκεκριμένα, τα κράματα αλουμινίου-χαλκού(Al-Cu)-2xxx, τα κράματα αλουμινίου-μαγνησίου(Al-Mg)-5xxx, τα κράματα αλουμινίου-μαγνησίου-πυριτίου(Al-Mg-Si)-6xxx, τα κράματα αλουμινίου-ψευδαργύρου(Al-Zn)-7xxx και τα κράματα αλουμινίου-λιθίου(Al-Li) περιλαμβάνουν υλικά που χρησιμοποιούνται σε δεξαμενές αποθήκευσης υδρογόνου λόγω των ιδιοτήτων τους.

Αν και τα κράματα αλουμινίου υψηλής αντοχής έχουν επιθυμητές ιδιότητες για τις δεξαμενές υδρογόνου, υποφέρουν από ψαθυροποίηση υδρογόνου (Hydrogen Embrittlement) όταν έρχονται σε επαφή με υδρογόνο, με αποτέλεσμα να παρατηρείται μείωση στις μηχανικές τους ιδιότητες και κίνδυνος σχηματισμού ρωγμών πριν από το αναμενόμενο σημείο. Η ψαθυροποίηση υδρογόνου προκύπτει από τη διάχυσή μέσα στο υλικό και την παγίδευση ατόμων υδρογόνου, η οποία οδηγεί σε εργοδιάβρωση. Έχουν προταθεί διάφορα μοντέλα για να εξηγήσουν αυτό το φαινόμενο και υπάρχουν διαθέσιμες τεχνικές για τη δοκιμή των υλικών και την πρόληψη της ψαθυροποίησης υδρογόνου. Εκτός από αυτά τα προληπτικά μέτρα, μπορούν να χρησιμοποιηθούν εναλλακτικά υλικά όπως κράματα με βάση το μαγνήσιο και το τιτάνιο, τα οποία είναι μία πολλά υποσχόμενη λύση.

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Acknowledgements

I am grateful to Prof. G.N. Haidemenopoulos, my thesis supervisor, for his valuable suggestions, guidance, and advice throughout this project.

Additionally, I would like to express my appreciation to Prof. N. Aravas and Prof. A. Kermanidis, who provided guidance throughout my studies and served on my thesis committee.

Finally, I want to thank my family and friends for their unwavering support.

1. Introduction

Transportation is a major contributor to global energy consumption, with internal combustion engines being responsible for a significant amount of this consumption. The reliance on non-renewable fossil fuels has led to environmental pollution and energy crisis, and researchers are seeking renewable alternatives to reduce our dependence on these fuels. Hydrogen is a promising option as it has a high energy density, is highly efficient, and produces no greenhouse gas emissions when used as a fuel. Its adoption in the automotive industry, which currently relies almost exclusively on gasoline, could have a significant impact. However, there are technical barriers to the widespread use of hydrogen, including the lack of safe, lightweight, and energy efficient ways to store it on board vehicles. While hydrogen has some advantages over electric vehicles in terms of refueling speed and simplicity, its tendency to ignite spontaneously due to its high diffusivity and low ignition energy makes storage a key consideration for hydrogen-powered vehicles in terms of both safety and performance.

The use of hydrogen as an energy source offers several advantages, including its ability to be generated via electrolysis using electricity produced from renewable sources, which allows hydrogen to meet energy demand. Additionally, hydrogen can be stored in large quantities for long periods without losing its energy content, unlike batteries. This means that hydrogen can be produced and stored on an industrial scale as a part of a green energy mix, and can be used as a backup energy source when needed.

Hydrogen can be used in conjunction with batteries as an energy source in the transportation industry. In this system, hydrogen provides the majority of energy storage while a small battery acts as a buffer to support regenerative braking and sudden power increases, as well as extend the lifespan of hydrogen fuel cells by adjusting to load changes. This method is already utilized in some commercially available vehicles, such as the Honda FCX Clarity. Hydrogen fuel cells have also been used for years to power forklifts safely and cleanly in indoor settings. While hydrogen has potential to be a key player in future clean energy solutions, further research and infrastructure improvements are necessary for it to reach its full potential.

Storing hydrogen can be challenging due to its low volumetric energy density and low boiling point. It is the lightest element, making it prone to being released into the atmosphere. In order to store hydrogen, it is necessary to either maintain low temperatures through cryogenic storage or utilize high-pressure tanks capable of storing the gas at 350-700 bar (35MPa to 70MPa). Another option for storing hydrogen is through adsorption or absorption, but these methods also require additional steps to release the hydrogen.

As shown in *Figure 1*, different methods for on-board hydrogen storage include compressed hydrogen gas, cryogenic and liquid hydrogen, sorbents, metal hydrides and chemical hydrides^[1].

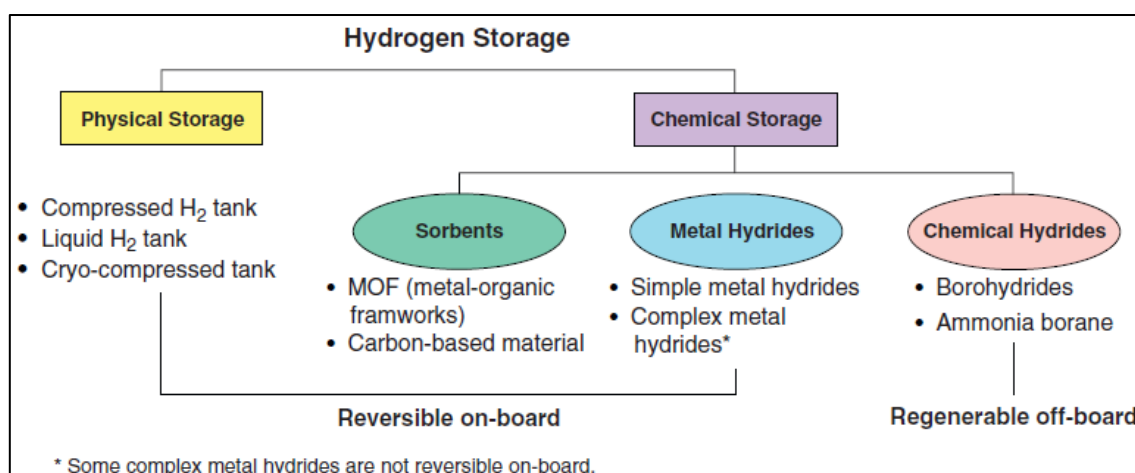


Figure 1: Classification of Hydrogen storage methods^[1]

In fuel cell vehicles, hydrogen is typically stored in *compressed tanks*. Augmenting the pressure inside the tank is a method of elevating the density of hydrogen. By increasing the pressure in the tank, it is enhanced the density of hydrogen. High Pressure Gaseous Hydrogen (HPGH₂) is stored in this way to achieve a higher density. The material used for the high-pressure tank is an important factor to consider, as it needs to be able to withstand the effects of hydrogen and be lightweight, cost-effective, and easy to handle^[2].

Increasing the storage pressure of hydrogen increases its density, which allows higher storage density in high pressure hydrogen (HPH₂) systems. The optimum storage pressure for on-board hydrogen systems in vehicles is typically between 35 and 70 MPa, considering factors such as the energy required for compression, driving range, and infrastructure investment costs. In 2003, the US Department of Energy announced the gravimetric and volumetric density requirements for on-board hydrogen supply systems not to be less than 6wt% H₂ and 60 kg H₂/m³, respectively to achieve a driving range of more than 500 km on a single fill, which were later revised in 2009 to be no less than 5.5 wt% H₂ and 40 kg H₂/m³, respectively by 2015^[3].

Cryogenic storage is another way to store hydrogen by increasing its volumetric density through liquefaction. This allows it to be stored in smaller, lighter containers as it requires less volume in this state. To keep hydrogen as a liquid, it must be kept below its boiling point of 20K. For this reason it needs effective insulation to maintain the efficiency of a Liquid Hydrogen (LH₂) tank, so that they are typically made with double walls and a vacuum between the inner and outer walls. Despite the higher volumetric density of LH₂ storage, it has some drawbacks. One issue is the high energy cost of liquefaction (about 35% is required to liquefy it). Another problem is that the LH₂ can evaporate, even in well-insulated tanks, leading to concerns about cost, energy efficiency, and safety. As a safety measure, pressure release valves have been implemented in recent years^[1].

High Pressure Gaseous Hydrogen (HPGH₂) storage is a popular method because of its fast filling and releasing rate, simplicity over Liquid Hydrogen (LH₂) storage. While liquefying hydrogen consumes 30-40% of its Lower Heating Value (LHV), compressing hydrogen to 35-70 MPa requires only 5-20% of its LHV. Furthermore, compressed hydrogen can be kept at ambient temperatures, whereas LH₂ requires special vacuum tanks to keep it at 20K^[4].

Cryo-compressed H₂, which combines cryogenic storage with compression, has been a popular area of research in physical hydrogen storage. This method includes pressurized liquid hydrogen, cooled compressed hydrogen gas, and systems that use both liquid and vapor phases of hydrogen. Lower temperatures lead to denser gas, enabling more hydrogen storage. Moreover, the cooling requirements for liquid hydrogen storage (20K) are not necessary, making this method more energy-efficient than LH₂ storage^[3].

Another type of hydrogen storage is *chemical hydrides*, which contain hydrogen chemically bound to other elements. They can store large amounts of hydrogen but are not easily rechargeable, so they are used in large systems that do not require onboard refueling, such as rockets and jets. Chemical hydrides come in two types: those containing metals and those made entirely of non-metals. Chemical hydrides made of non-metallic elements have higher energy densities than those containing metals because they consist of lighter elements^[1].

Compared to mechanical storage like compressed hydrogen, cryogenic storage, and cryo-compressed storage, *metal hydrides* generally offer a greater capacity for hydrogen storage in both volume and weight. Additionally, their capacity to function at low temperatures and pressures is important for fuel cell vehicles.

Figure 2 illustrates various hydrogen storage methods, including tanks with high pressure of 35 and 70 MPa, liquid hydrogen tanks, tanks with hydrogen-absorbing alloy tanks and chemical storage^[5].

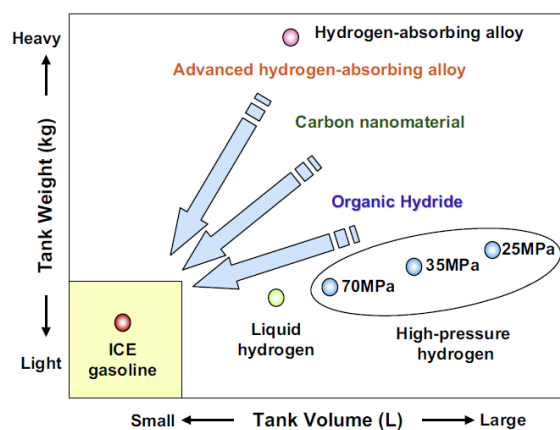


Figure 2: Technologies of storing hydrogen^[5]

This project focuses on the Compressed Hydrogen tanks and the materials that are used to construct them. Compared to other storage techniques, high-pressure hydrogen storage has been discovered to offer benefits in terms of hydrogen density, cost, and practical applications. Ensuring the storage of hydrogen is essential for its participation in the alternative energy

sources. As the world works towards decreasing emissions and shifting away from carbon-based fuels, hydrogen fuel cells offer a cleaner option for generating power. They have the potential to power a range of things, including electronic devices, transportation, aircraft, and even entire buildings.

It is also important to think about the entire hydrogen pathway (*Figure 3*), from its production to its utilization on-board vehicles^[5].

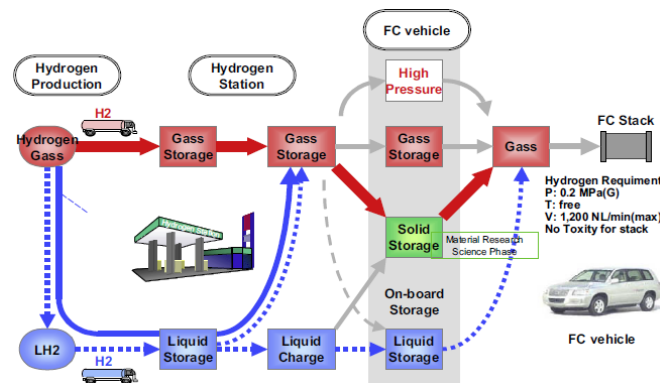


Figure 3: Entire hydrogen pathway from production to fuel cell^[5]

2. Materials for Hydrogen Tanks

Hydrogen can be stored in four types of pressure vessels, as shown in *Figure 4*, which can be cylindrical, polymorph, or toroidal in shape. The tanks are categorized as Type I, Type II, Type III, and Type IV based on their construction materials. Type I tanks are made of metal, while Type II tanks consist of a metallic liner reinforced with a fiber resin composite wrap. Type III and Type IV tanks are entirely made of composite materials, with the former having a metallic liner wrapped in carbon fibers within a polymer matrix, and the latter having a plastic liner. Currently, the most prevalent hydrogen tank in use is the Type III composite storage tank, with an inner aluminum liner^[6].

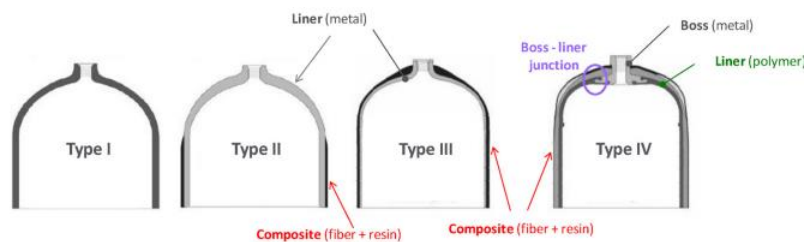


Figure 4: Various categories of pressure vessels based on their construction materials^[6]

Compressed hydrogen tanks are used to store hydrogen gas at high pressures, typically between 350 and 700 bar. The goal is to store as much hydrogen as possible in a given volume, so that it can be used as a fuel source for vehicles or other applications. There are various types of compressed hydrogen tanks as mentioned above.

1. Type I: They are made of either steel or aluminum with usually cylindrical shape and they are designed to withstand high pressures. They can store hydrogen at around 70MPa pressure and they are the most common and cost-effective type of tank.
2. Type II: They are made of steel and have a glass fiber composite overwrap, present in equal amount in the material. They are designed to lightweight and have a higher capacity than Type I tanks with the highest pressure tolerance among the four categories.
3. Type III: They are full composite wrap with metal liner. The most of load is carried by the composite structure (carbon fiber composite). Although they have demonstrated reliability at a working pressure of 45MPa, they still encounter challenges when doing tests at 70MPa.
4. Type IV: They are fully composited of composites, with a liner typically made of a polymer like High Density Polyethylene (HDPE) and carbon fiber or carbon-glass composites used for carrying the load. They can withstand pressures up to 100MPa.

Each type of tank has its pros and cons, depending on the application and specific requirements. However, all compressed hydrogen tanks must meet safety standards to ensure that the stored hydrogen is safely contained and does not pose a danger to people or the environment.

Tanks are commonly made from a variety of materials, including metallic, polymer, and composite materials. Metallic parts used in tank construction may include Al-alloys 6061 and 7060, as well as steel such as inox and Chrome Molybdene. Polymer parts, made from polyethylene or polyamide based polymers. Composite materials made from glass, aramid or carbon fiber embedded in epoxy resin are also commonly used for tank construction. Carbon fibers are preferred for applications requiring 35MPa or more, and epoxy resins are often chosen for their good mechanical properties, stability, and compatibility with the filament winding process. Also, tanks can be manufactured using three methods depending on their type (I, II, III): by deep-drawing plates to form the shape, by heating billets to carry out the shape, or for tubes, the neck then is formed by hot-spinning.

After forming, using heat treatments are achieved the desired mechanical properties^[6].

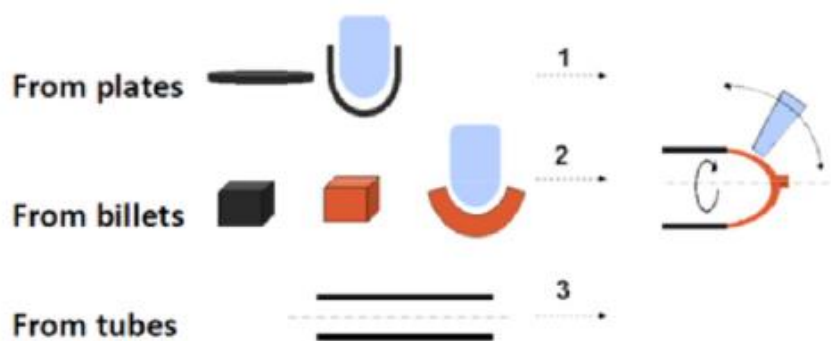


Figure 5: Different ways to manufacture the metallic pressure tanks from plates, billets and tubes^[6]

Using plates, billets, or tubes can be manufactured the metallic tanks. Polymer liners for Type IV pressure tanks, on the other hand, can be created by rotomolding, blow molding, or welding injected domes to an extruded polymer tube. Metal components may be added during the

forming step or attached by adhesive to the liner during a secondary phase. Composite pressure tanks are produced by winding filaments embedded in resin. Quality controls are performed for each technology to ensure the materials and manufacturing process meet specific standards. The pressure vessels are tested by exposing them to 1.5 times the working pressure.

In *Table 1* is presented a summary of the gravimetric densities and costs of four distinct categories of hydrogen storage tanks, by Rivard et al.^[7]. The gravimetric density denotes the weight of hydrogen concerning the entire weight of a hydrogen tank when it is entirely filled. Compared to Type I tanks, Type II tanks have a lower total containment weight. In contrast, Type III tanks come with considerably higher costs when compared to Type I and Type II tanks. Type IV tanks have comparable costs to Type III tanks and their weight is lower.

Table 1: Cost and gravimetric density of Type I, II, III and IV tanks^[7]

Type	Materials	Maximum pressure [bar]	Cost [\$/kg]	Gravimetric density [wt %]
I All-metal construction	Austenitic steels or aluminium alloys	300	83	1.7
II Metallic liner hoop wrapped by composite	Aluminium alloys liner and glass-, aramid- or carbon-fibre composites	300	86	2.1
III Metallic liner fully wrapped by composite	Aluminium alloys liner and glass-, aramid- or carbon-fibre composites	Mature for 350; development for 700	700	4.2
IV All-composite construction	Polyethylene or polyamide based polymers liner and glass-, aramid- or carbon-fibre composites	Mature for 350; development for 700	633	5.7

There are several properties that are required for compressed hydrogen storage:

1. *High storage density*: the goal of compressed hydrogen storage is to store as much hydrogen as possible in a given volume, so that it can be used as a fuel source for vehicles or other applications.
2. *Safety*: the storage tank should have the capability to endure various conditions such as alterations in temperature and pressure, as well as impact and vibration.
3. *Durability*: the storage tank should have the capability to endure the conditions of long term storage, including exposure to temperature and pressure changes, as well as vibration and impact.
4. *Low cost*: the storage tank must be inexpensive to manufacture and maintain, in order to make hydrogen storage a viable option for large-scale commercial use.

5. *Low weight*: the storage must be lightweight to minimize the weight of the hydrogen storage system and make it practical for use in vehicles and other portable applications.
6. *Corrosion Resistance*: the storage tank must be resistant to corrosion and degradation to ensure the long-term resistance of the stored hydrogen.
7. *Temperature stability*: the storage tank must be able to maintain its structural integrity over different temperatures, to ensure the safe storage of hydrogen under a variety of conditions.
8. *Easy to transport*: the storage tank must be easy to transport, in order to make it practical for use in vehicles and other portable applications.

The material of the tank is a critical factor in the storage of compressed hydrogen. It should be lightweight, affordable, and strong enough to withstand the necessary stress and strain, as well as meet safety specifications. Furthermore, the material should possess sufficient thermal conductivity to regulate the exothermic heat produced when the filling process takes place.

When designing pressure tanks, the following factors should be taken into consideration: the intended use, the test and operational pressures, external stresses (such as mechanical and chemical impacts), the expected number cycling life, the safety factor under both static and dynamic conditions, and the effects of conditions during operation on the materials and structure of the tank. *Figure 6* illustrates the main stresses that are typically considered for metallic cylinders or liners^[6].

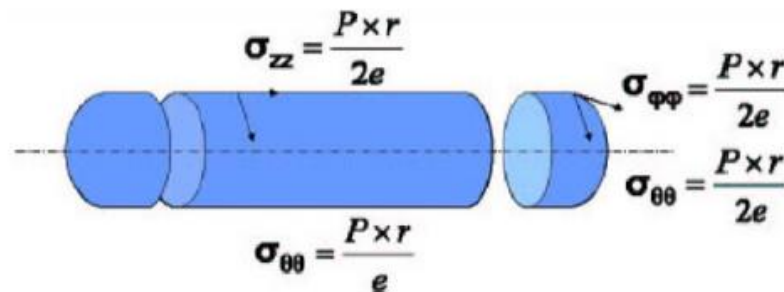


Figure 6: Stresses in metallic pressure tanks^[6]

The tensile strength of materials that are used for hydrogen storage tanks can range from 50MPa for Aluminum to over 1100MPa for high-strength steel. Alternative materials, have ever higher tensile strength of up to 2410MPa with density only 2370kg/m³. The progress in technology has resulted in the creation of lightweight composite cylinders that can endure a pressure of up to 80MPa. This permits hydrogen to possess a volumetric density of 36kg/m³, roughly half of its density in the liquid state at the normal boiling point.

The ideal material for a high-pressure cylinder must possess high tensile strength and low density, while preventing hydrogen diffusion or any reactivity with it. High-pressure cylinders are usually made of austenitic stainless steel (e.g., AISI 316 and 304, and AISI 316L and 304L

at temperatures above 300°C to prevent carbon grain-boundary segregation), copper, or aluminum alloys that demonstrate considerable resistance to hydrogen effects at room temperature. As the cylinder's internal pressure increases, the volumetric density of hydrogen increases too, reaching its maximum at pressures above 1000bar, based on the material's tensile strength. However, as pressure increases, the weight of the hydrogen inside the cylinder decreases, leading to the highest gravimetric density at zero overpressure. The trade-off between the increase in volumetric storage density and pressure is a limitation of pressurized gas systems. *Figure 7*^[8] presents the volumetric density of hydrogen within a cylinder as a function of gas pressure.

The best material for a high-pressure cylinder is one that has a high-pressure cylinder is one that has a high tensile strength, low density and does not react with or allow diffusion of hydrogen. Most of high-pressure cylinders have been made from austenitic stainless steel (such as AISI 316 and 304 and AISI 316L and 304L above 300°C to avoid carbon grain-boundary segregation), Cu or Aluminum alloys which are largely resistant to hydrogen effects at room temperature. However, as pressure inside the cylinder increases, the volumetric density of hydrogen also increases, reaching a maximum at pressures above 1000bar, depending on the tensile strength of the material. However, as pressure increases the weight of the hydrogen stored in the cylinder decreases, and the maximum gravimetric density is found for zero overpressure. This trade-off between the increase in volumetric storage density is a limit of pressurized gas systems. *Figure 7* shows the volumetric density of hydrogen inside a cylinder as a function of gas pressure^[8].

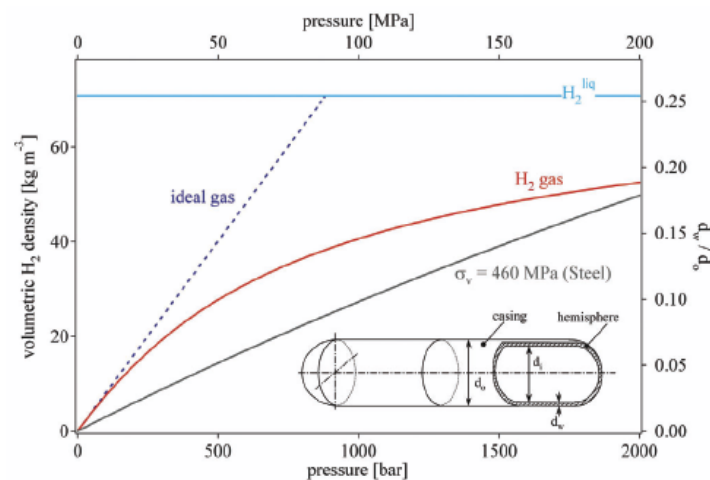


Figure 7: Volumetric density of compressed hydrogen gas as a function of gas pressure^[8]

Nowadays, more and more auto manufacturers apply aluminum in cars. Around 30.000 parts or the car are made of aluminum. It is crucial for the car to be structurally sound, but it must also be lightweight, cost efficient to make, corrosion resistant and have attractive surface finishing treatments. Aluminum is a material that meets these requirements due to its various beneficial properties and it is a choice for use in hydrogen storage tanks.

The most important factor to use aluminum in the automotive industry is its *light weight and durability*. The *high strength-to-weight ratio* of aluminum makes it an ideal choice for reducing the weight of vehicles, which is a key goal in the industry in order to achieve the emissions targets from the government. Research has shown that using aluminum in cars can help to

reduce vehicle weight, improve fuel economy and lead to lower emissions. Aluminum alloys have good strength-to-weight ratio, which means that they can withstand high pressures while keeping the weight of the tank low.

One of the major benefits of using aluminum in the automotive industry is its *formability*. Aluminum has a high level of formability, which means it can be easily shaped and worked into different shapes, such as cylindrical or spherical tanks. It is also *resistant to corrosion*, which makes it a durable material to treat it. Additionally, aluminum is found in different ways of formation including sheet, coil, plate, tube, pipe, channel, beam, bar, and angle. This flexibility allows it to be used in many applications to the automotive industry in which is necessary different parameters such as size, shape, yield strength, surface treatment, or corrosion resistance.

Aluminum is easy to work with and it has the *ability to alter it through different fabrication treatments*, including work and precipitation hardening, drawing, annealing, casting, molding, and extrusion, to improve its performance and versatility. Aluminum alloys are *easily welded* and can be joined together to form tanks. Advances in welding technology have made it easier and safer to join aluminum.

Also, aluminum alloys have *good thermal conductivity* which helps in dissipating the heat during high pressure and high temperature operations.

To aluminum can be added different alloying elements to improve its properties, such as strength, electrical conductivity, and corrosion resistance. This step can improve its use in auto manufacturing. Aluminum alloys are classified into series based on their main alloying elements. As it was mentioned, Aluminum alloys are suitable materials for hydrogen storing tanks, specifically the Al-Cu alloys-2xxx, the Al-Mg alloys-5xxx, the Al-Mg-Si alloys-6xxx, the Al-Zn alloys-7xxx and Al-Li alloys include materials that are used in hydrogen storage tanks because of their properties.

The 2xxx series of aluminum alloys are heat treatable alloys, they are aluminum/copper alloys, with copper additions ranging from 0.7 to 6.8%. These alloys have a high strength, exceptional performance, making them ideal for use in aerospace and aircraft applications due to their high strength over different temperatures. Although some of these alloys are vulnerable to hot cracking and stress corrosion cracking, making them difficult to weld using arc welding processes. The ultimate tensile strength of 2xxx series alloys ranges from 27 to 62 ksi(185 to 430MPa).

The 5xxx series of aluminum alloys are non-heat treatable alloys. they are aluminum/magnesium alloys with magnesium additions ranging from 0.2 to 6.2%. They are readily weldable and are used in a variety of applications such as shipbuilding, transportation, pressure vessels, bridges, and buildings. Alloys of the 5xxx series with more than 3.0% magnesium should not be used to temperatures more than 150 degrees. Their ultimate tensile strength varies between 18 to 51 ksi(125 to 350MPa). Compared with all non-heat treatable alloys they have the highest strength.

The 6xxx series of aluminum alloys are heat treatable alloys, they are aluminum/magnesium/silicon with magnesium and silicon additions of around 1.0%. They are widely used in the welding and fabrication industry, particularly in the form of extrusions, and are found in many structural components. The existence of magnesium and silicon to aluminum creates a compound Mg_2Si , which makes the material to be heat treated to improve its properties. These alloys are prone to solidification cracking and for arc welding should be used filler material to specific amounts to prevent hot cracking. Their ultimate tensile strength ranges from 18 to 58 ksi(125 to 400MPa).

The 7xxx series aluminum alloys are heat-treatable alloys, they are aluminum/zinc alloys with zinc levels ranging from 0.8 to 12%(usually 4-6%), 1-3% magnesium and possibly up to 3% copper. They have high strength and are used in applications such as aircraft, aerospace engineering, military equipment and nuclear power equipment because of their high strength-to-weight. This makes them preferable materials for use them to application to reduce fuel consumption and environmental impact. The strength of these alloys is attained through the creation of a large number of precipitates during an aging thermal treatment, which results in a high density of approximately $10^{24}m^{-3}$ [9]. Some alloys in this series are not suitable for arc welding, while others can be welded using filler alloys from the 5xxx series, such as the commonly welded alloy 7005. with ultimate tensile strength ranging from 32 to 88 ksi(220 to 620 MPa).

Al-Li (Aluminum-Lithium) alloys are a group of light-weight metal alloys composed of aluminum and lithium. By using Al-Li alloys in metal components, a 20% reduction in weight is expected. They are used in many industries including aerospace, automotive, and sports equipment because of their combination of high strength, low density, and corrosion resistance. Al-Li alloys also have a higher elastic modulus, lower thermal expansion, and better stiffness compared to conventional aluminum alloys. Despite the fact that Al-Li alloys have a certain level of resistance to fatigue crack propagation, there is a potential for their corrosion resistance to be enhanced. These alloys are relatively more costly compared with other aluminum alloys and extra precautions must be taken during fabrication, segregation, recycling, and disposal to ensure safety^[10].

Some specific examples of materials that are used for hydrogen tanks are:

5052 Al-alloy: 5052aluminum alloy sheet used for fuel tanks has high strength, especially high fatigue strength. Except of magnesium contains small amounts of manganese, chromium, beryllium, titanium, and other elements. These elements, particularly chromium and manganese, improve the sheet's resistance to stress corrosion cracking, increase the strength of the base metal and welds, and reduce the likelihood of welding cracks. This makes the fuel tank resistant to cracking under impact and ensures the safety of the vehicle. In addition, aluminum alloy is not easily flammable and has excellent explosion-proof properties. In the following tables are shown the chemical composition (*Table 2*) and the mechanical properties (*Table 3*) of 5052 Al-alloy. The fuel tank for automobiles is usually made of 5052 aluminum alloy, this material is chosen because it is lightweight, low density, and can hold a large volume.

Element	Si	Fe	Cu	Mn	Mg	Cr	Zn	Al
Standard Value	max 0.25	max 0.4	max 0.1	max 0.1	2.2-2.8	0.16~0.35	0.1	Balanced

Table 2: Chemical Composition of 5052Al-alloy

Property	Yield Strength σ_Y (MPa)	Ultimate Strength σ_{UTS} (MPa)	Elongation (%)
Value	175	270	8

Table 3: Mechanical properties of 5052Al-alloy

5083 Al-alloy: The 5083 aluminum alloy has high strength-to-weight ratio, good corrosion resistance, and super-elasticity. The strength of Al-Mg alloys comes from magnesium solid solution strengthening, which increases with the amount of magnesium. Adding other alloying elements, such as Sc, La, Ce, and Y, can also increase strength. Erbium (Er) has been found to be an ideal alloying element for aluminum alloys, improving material properties with small Er additions. The strength of 5083 aluminum alloy is due to the Al_3Er phase formed in the alloy. It is generally believed that after long-term use, 5083 aluminum alloy will soften and require annealing to stabilize its properties. Mechanical properties, corrosion resistance and microstructure can be changed through heat treatment. Annealing treatment affects the dislocation configuration in the matrix and the interface of the second phase and as a result influenced the mechanical and corrosion resistance properties. To enhance both properties, annealing temperature and time should be optimized^[11]. This alloy should not be used in temperatures above 65°C. In the following tables are shown the chemical composition (*Table 4*) and the mechanical properties (*Table 5*) of 5083 Al-alloy.

Element	Si	Fe	Cu	Mn	Mg	Cr	Zn	Al
Standard Value	max 0.4	max 0.4	max 0.1	0.4-1	4-4.9	0.05-0.25	0.1	Balanced

Table 4: Chemical Composition of 5083Al-alloy

Property	Yield Strength σ_Y (MPa)	Ultimate Strength σ_{UTS} (MPa)	Elongation (%)
Value	230	315	16

Table 5: Mechanical properties of 5083 Al-alloy

6061 Al-alloy: 6061 Aluminum is an alloy consist of aluminum, magnesium, and silicon. It is known for its strong yet lightweight properties. It has good mechanical properties, exhibits good weldability, formability, workability and corrosion resistance. Precipitated phases are

produced due to heat treatment to various degrees. The precipitate type, density and size affect the hardness and strength of this alloy. It is one of the most common alloys of aluminum for general-purpose use. In the following tables are shown the chemical composition (*Table 6*) and the mechanical properties (*Table 7*) of 6061 Al-alloy.

Element	Si	Fe	Cu	Mn	Mg	Cr	Zn	Al
Standard Value	0.4-0.8	Max 0.7	0.15- 0.40	max 0.15	0.8- 1.20	0.04-0.35	0.25	Balanced

Table 6: Chemical Composition of 6061 Al-alloy

Property	Yield Strength σ_Y (MPa)	Ultimate Strength σ_{UTS} (MPa)	Elongation (%)
Value	275	310	12-17

Table 7: Mechanical properties of 6061 Al-alloy

7075 Al-alloy: The 7075 Aluminum alloy is a material comprised of aluminum and primarily zinc. This alloy boasts remarkable mechanical properties and boasts toughness, high strength, good ductility and resistance to fatigue. Despite being more prone to embrittlement due to microsegregation compared to other aluminum alloys, it still has superior corrosion resistance compared to alloys from the 2000 series. 7075 Aluminum is widely used in high-stress structural applications. In the following tables are shown the chemical composition (*Table 8*) and the mechanical properties (*Table 9*) of 7075 Al-alloy.

Element	Si	Fe	Cu	Mn	Mg	Cr	Zn	Al
Standard Value	max 0.4	max 0.5	1.2-2	max 0.3	2.1-2.9	0.18-0.28	5.1-6.1	Balanced

Table 8: Chemical Composition of 7075 Al-alloy

Property	Yield Strength σ_Y (MPa)	Ultimate Strength σ_{UTS} (MPa)	Elongation (%)
Value	500	570	11

Table 9: Mechanical properties of 7075 Al-alloy

The steps for creating high-pressure hydrogen storage tanks using aluminum alloys can include the following:

1. *Design and modeling*: The tank design is modeled and optimized for specific application requirements, such as pressure, temperature and corrosion resistance.
2. *Material Selection*: The appropriate aluminum alloy is selected based on the design requirements and material properties such as strength, formability and weldability.
3. *Fabrication*: The tank is fabricated using the chosen aluminum alloy, typically through welding or other joining methods.
4. *Testing*: The tank is tested for strength, leak tightness and other performance characteristics to ensure it meets safety and performance requirements.
5. *Certification*: The tank is certified for use in the specific application, such as for use in vehicles or for stationary storage.
6. *Maintenance and Inspection*: Regular maintenance and inspection of the tank necessary to ensure it continues to function safely and efficiently over its service life.

Safety is a concern when it comes to pressurized cylinders. It is believed that in the future, high-pressure vessels will consist of three parts: an inner polymer liner over-wrapped with a carbon-fiber composite (which is the stress-bearing component) and an outer part of an aramid-material capable of withstanding mechanical and corrosion damage.

2.1. Effect of Chemical Composition on properties of Aluminum alloys

Alloying elements when added to aluminum alloys affect some processes such as, precipitation hardening (age hardening), dispersion hardening, grain refining, changing of intermetallic phases, prevention of grain growth at elevated temperatures (e.g. during annealing), fracture resistance and other properties. The effect of the most important alloying elements on the mechanical properties of the materials is presented below.

Silicon, Si (up to 17%):

It improves the castability of aluminum alloys by improving the fluidity of molten aluminum-silicon alloys and reducing shrinkage of molten aluminum-silicon alloys. It also improves the strength and the resistance to fracture of the alloy and when precipitates as pure Si is hard and increases corrosion resistance. Also, when the Si is increased it is observed that the ultimate tensile strength of alloys is increased and their density is decreased^[12]. In combination with silicon and magnesium allows the alloy to be strengthened by precipitation hardening (wrought aluminum-magnesium-silicon alloys (6xxx)).

Copper, Cu (up to 6.5%):

It improves the tensile strength, fatigue strength and hardness of alloys through solid solution hardening. Alloys can be strengthened by heat treatments through precipitation (wrought

aluminum-copper alloys (2xxx)). However, it reduces the ductility of the alloy and it decreases corrosion resistance. The increase of *copper* in the alloy makes stable some phases like $\text{Al}_5\text{Cu}_2\text{Mg}_8\text{Si}_6$ and Al_2Cu which promotes the precipitation hardening. The increase of both Si, Mg and Cu improves the durability but reduces the extrudability^[13].

Magnesium, Mg (up to 10%):

It improves strength and hardness of alloys by solid solution hardening without losing to ductility (aluminum-magnesium wrought alloys (5xxx)). In combination with silicon or zinc, alloys can be strengthened by precipitation hardening (aluminum-magnesium-silicon wrought alloys (6xxx), aluminium-zinc-magnesium wrought alloys (7xxx)). The increase of Mg improves the tensile strength. Furthermore, with increased amount of magnesium in the alloy, the average values of the Dendrite Arm Spacing and grain size reduced in cast condition^[14].

Manganese, Mn (up to 1.5%):

It affects strength and hardness of alloys (aluminum-manganese (3xxx) wrought alloys) by solid solution hardening and dispersion hardening mechanisms. Also, it improves low cycle fatigue resistance and corrosion resistance. When the aluminum alloy contains iron takes place the modification of Al_5FeSi intermetallic inclusions from platelets to cubic $\text{Al}_{15}(\text{MnFe})_3\text{Si}_2$, as a result it is improved the ductility of the material.

Zinc, Zn (up to 8%):

In combination with magnesium or magnesium-copper, the alloy can be strengthened by precipitation hardening heat treatment (aluminum-zinc-magnesium wrought alloy (7xxx)). It also, it is decreased the stress corrosion cracking.

Chromium, Cr (up to 0.3%):

Prevents grain growth at elevated temperatures (during heat treatment, etc.) and recrystallization in Al-Mg-Si alloys during heat treatment. The modification of Al_5FeSi intermetallic inclusions from platelet to cubic form (similar to the effect of manganese) improves ductility and toughness of alloys containing iron and silicon. Chromium also reduces stress corrosion susceptibility^[15].

Iron (up to 0.8%):

Aluminum alloys often contain iron as an impurity, which can have negative effects on the castability and ductility, especially in aluminum-silicon alloys. Iron has a notable impact on the solidification of aluminum because it has a strong tendency to partition. Although iron is usually present as a minor impurity at around 0.2 wt%, it tends to combine with aluminum and silicon to create intermetallic compounds, which can alter the sequence of solidification and extrudability^[16].

Zirconium:

Zirconium when is added to aluminum alloys creates a fine precipitate of intermetallic compounds that inhibit crystallization of grains^[17].

3. Problems associated with the storage of H₂ under high pressure

Hydrogen is a safe fuel when the appropriate engineering controls are in place. It has several properties that make it safer than other fuels, such as being non-toxic and quickly dissipating into the atmosphere when released. However, it has specific hazards that requires additional safety measures, such as a lower ignition energy and a range of flammable concentrations in the air. This means that proper ventilation and leak detection are important for hydrogen systems, as well as the use of specialized flame detectors.

The development of fuel cell vehicles is limited by the low density of hydrogen and the resulting low range of the vehicles. Hydrogen has only 1/10 of the energy of gasoline per unit volume, meaning that it is difficult to have enough hydrogen on board to achieve a range comparable to fossil fuels. Improving the performance of hydrogen storage and the amount of hydrogen that can be stored on board is therefore a factor challenge for the adoption of hydrogen in the automotive industry.

Storing in its low-pressure gaseous form is preferable, but vehicles do not have the capacity to store enough hydrogen in this form. Therefore, it is necessary to compress it.

Storage tank failures can be attributed to multiple factors, such as material fracture, pressure build-up due to leaks or failure of pressure relief systems, and physical threats like hydrogen permeation and embrittlement. The permeability of both composite and metallic materials used in tanks may rise with an increase in temperature, which could result in the gathering of hydrogen gas and the development of micro cracks in the material. In the case of metallic materials, hydrogen embrittlement may affects the load-forces that the material can withstand, leading to premature failure. Moreover, the transfer of heat through conduction, convection, and radiation poses a complex challenge in the design of storage tanks.

The materials used in hydrogen systems must also be carefully selected, due to some metals are affected negatively when exposed to hydrogen. Staff training and regular testing for leaks and other issues are also necessary to ensure the safe use of hydrogen. Despite these precautions, hydrogen has already been successfully used in a variety of applications, demonstrating its potential as a safe, clean, and renewable fuel for the future.

The problems associated with the storage of hydrogen under high pressure are^[5]:

1. *Safety*: High-pressure hydrogen storage tanks can be dangerous if not properly designed, maintained and stored. A leak of failure in the tank can be pose a risk of explosion or fire.
2. *Leakage*: High-pressure hydrogen tanks can develop leaks over time, which can result in the loss of stored hydrogen and be dangerous if the hydrogen leaks into an enclosed space.
3. *Corrosion*: High-pressure hydrogen storage tanks are made of materials that can be prone to corrosion, especially if they are exposed to moisture or other chemicals.
4. *Cost*: High-pressure hydrogen storage tanks are relatively expensive to manufacture and maintain.

5. *Durability*: High-pressure hydrogen storage tanks are subject to work and tear over time, which can make them less reliable and less durable.
6. *Temperature*: High-pressure hydrogen storage tanks require specific temperature control to maintain the integrity of the tanks.
7. *Transport*: Transporting high-pressure hydrogen tanks can be difficult and dangerous, as they are large, heavy and potentially dangerous if not handled properly.
8. *Regulations*: The storage and transport of hydrogen fuel in high-pressure tanks are subject to government regulations, which can vary depending on location, and may change over time.

According to Kircher et al ^[7], the adiabatic expansion energy of LH₂ and CcH₂ is 6 to 15 times lower than that of compressed GH₂. This means that in the event of a sudden pressure vessel failure, the stored energy of LH₂ and CcH₂ will be released quicker, potentially reducing the risk of severe storage failures such as tank bursts. Therefore, the LH₂ and CcH₂ storage methods may be safer than the compressed GH₂ method in the case of sudden pressure tank failure during refueling.

When designing a pressure tank, it is important to consider how the gas inside the tank will interact with the material of the tank and how the operating conditions may affect them. This is necessary in order to reduce the danger of failure because of bursting or leaking.

The metallic materials near hydrogen are affected by *hydrogen embrittlement*, causing a reduction in mechanical properties and the potential for premature cracking. This happens because of dissolution and trapping of hydrogen atoms, which has as result stress corrosion cracking. To deal with this problem, various efforts have been made to improve our understanding of the mechanisms of hydrogen embrittlement, improve the manufacturing of alloys, and optimize the assembly of components. There are also several testing methods that can be used to evaluate the fracture toughness of materials (such as ASTM 1681, ASTM 1820, and methods B and C of ISO 11114-4 and ANSI/CSA).

To maintain the efficiency and reliability of fuel cells, it is crucial to ensure high-purity hydrogen when using polymer parts, (such as a liner for type IV pressure tanks). Water is one of the main compounds that can be released from a polymer liner. The chemical nature of the polymer material determines the amount of water that it can be contained. All gases can infiltrate polymers by dissolving and diffusing gas molecules within the polymer matrix, with hydrogen being particularly susceptible due to its small molecular size. There are standards and regulations to ensure the maximum allowable rate of permeation for safety reasons. Emptying a tank hastily can cause the liner's deformation when the pressure is released, which depends on the maximum pressure attained in the cylinder during the emptying process. To avoid this, residual pressure valves should be utilized. During the filling and emptying processes, the tank's structure (specifically the polymer liner) is exposed to high temperatures (ranging from 65 to

85°C) and low temperatures (ranging from -40 to -60°C, based on standards). Therefore, careful selection of materials is necessary to prevent degradation and the possibility of leaks.

Composite wrappings,(types II, III, and IV pressure tanks), can be damaged due to pressure loads, environmental factors, and mechanical impacts during operation (such as monotonic pressurization and filling/emptying cycles). Damage mechanisms that may occur in these types of composites include fiber breaks, delamination, and matrix cracking.

Ensuring safety is a crucial consideration for the widespread use of hydrogen in the automotive industry. Some potential hazards associated with High Pressure Gaseous Hydrogen (HPGH₂) include vessel explosions, gas leaks, temperature increases during filling, and Hydrogen Embrittlement (HE) at room temperature. High-pressure, high-purity hydrogen at room temperature can negatively affects the mechanical properties of metals, leading to Hydrogen Embrittlement, a phenomenon in which hydrogen diffuses into many metals and causes undesired effects. Hydrogen can interact with the crystal lattice of some materials(such as iron, steel, nickel, titanium, vanadium, zirconium, silicon) that are used in pressure vessel design. The diffusion of hydrogen into materials can result in hydrogen embrittlement, stress corrosion cracking, hydrogen-induced cracking, and other adverse effects, which may lead to fracture and failure of the material. The presence of hydrogen atoms can cause localized plastic deformation and increase the rate of crack propagation in the metal, elevating the danger of sudden failure of high-pressure hydrogen tanks^[18].

Hydrogen embrittlement affects material's mechanical properties, including the fracture toughness, strength, fatigue strength and/or ductility. These properties can be degraded due to the presence of atomic hydrogen. There are three types of hydrogen embrittlement: hydrogen environmental embrittlement, internal hydrogen embrittlement, and hydrogen reaction embrittlement. Hydrogen environmental embrittlement is caused by both exposure to hydrogen and applied stress, and is often initiated at surface defects. Hydrogen reaction embrittlement is caused by atomic hydrogen reacting metallic materials at high temperature and pressure. To reduce the risk of hydrogen embrittlement failure can be used any of these three factors: by selecting suitable materials, reducing hydrogen gas pressure, or decreasing external applied stress.

Metallurgical interaction between atomic hydrogen and the structure of a material limits its capacity to react, deform, or elongate when subjected to stress. This can cause the material to become brittle under stress, resulting in fracture occurring at a significantly lower level of strain or stress than anticipated. The negative impact of hydrogen embrittlement is about the materials' ability to diminish the fracture strength of the material, and this effect becomes more pronounced as the strength of the material increases. The atomic level of embrittlement happens at concentration of hydrogen at 10ppm^[19]. Hydrogen atoms segregate at defect areas in the material, dislocations, vacancies etc.. Due to residual or imposed stress, hydrogen atoms have a tendency to move into the atomic structure of the storage material. When the hydrogen atoms are connect with the storage material, the hydrogen atoms are gathered locally and they forme hydrogen molecules. Over time, hydrogen atoms near defects diffuse to the defect areas and as

a result the hydrogen gas pressure increases. When gas pressure passes the material's critical strength hydrogen-induced cracking occurs.

According to *Figure 8*, hydrogen enters in the material in liquid or gaseous form and moves in the material through different ways, leading to material's degradation and failure. The hydrogen that dissolves in the material can exist in atomic or molecular form, or in a combination of both forms once it has been absorbed by the material. These large molecules are unable to pass through the material, so pressure appear to build up at points of crystallographic defects and discontinuities (dislocations and vacancies, voids, inclusion/matrix contacts resulting in small cracks. Whether or not this hydrogen causes crack depends on these factors: material's strength, external stresses, pressure and temperature^[18].

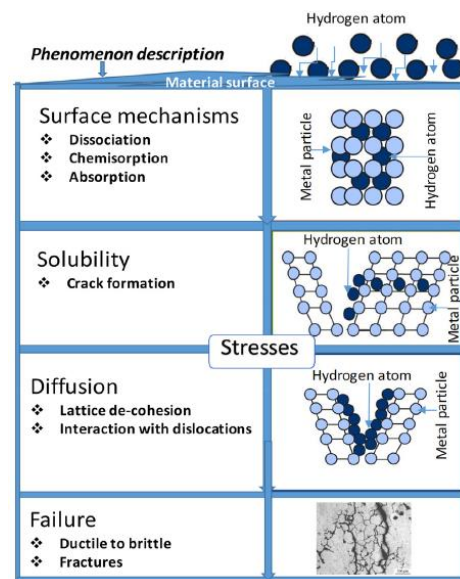


Figure 8: Hydrogen embrittlement mechanism^[18]

Hydrogen evolution reactions can occur at the cathode that forms in the crack because of mass transfer of oxygen at the crack is limited. This leads to the accumulation of hydrogen atoms at the top of the crack, increasing the hydrogen pressure and making the crack more likely to grow. While the hydrogen storage tanks in vehicles are typically not exposed to humid environments, the working conditions of aluminum alloys are often humid.

The susceptibility of a material to hydrogen embrittlement is affected by the presence of alloying elements. The more alloying elements that are dissolved in the supersaturated solid solution, the more susceptible the material will be to stress corrosion. For ternary and higher aluminum alloys, the stress corrosion sensitivity is also influenced by the ratio of these elements. The addition of alloying elements modifies the structure and electrochemical properties of the aluminum alloy and may interact with hydrogen. By influencing the presence and activity of hydrogen, the material's sensitivity to hydrogen embrittlement can be significantly improved, which is critical for enhancing the properties of aluminum alloys. Additionally, the depth of hydrogen penetration into the alloy also affects the occurrence of hydrogen embrittlement.

Hydrogen embrittlement is a major concern for aluminum alloys used in various industries, including automotive. It can cause the fracture of aluminum alloys and is a common cause of failure. The damage of aluminum alloys can result from initiation and propagation of cracks. Finding ways to limit hydrogen embrittlement is an ongoing research field. Aluminum alloys with low weight and favorable mechanical properties are a preferred choice for hydrogen storage tanks. Cracks between the bottle cap and the wedge, as shown in *Figure 9*, can increase the likelihood of hydrogen embrittlement. The lack of a clear reason for material failure during hydrogen embrittlement makes it a challenging problem to solve. Solving the issue of hydrogen

embrittlement is important for improving the effectiveness and reliability of aluminum alloys^[20].

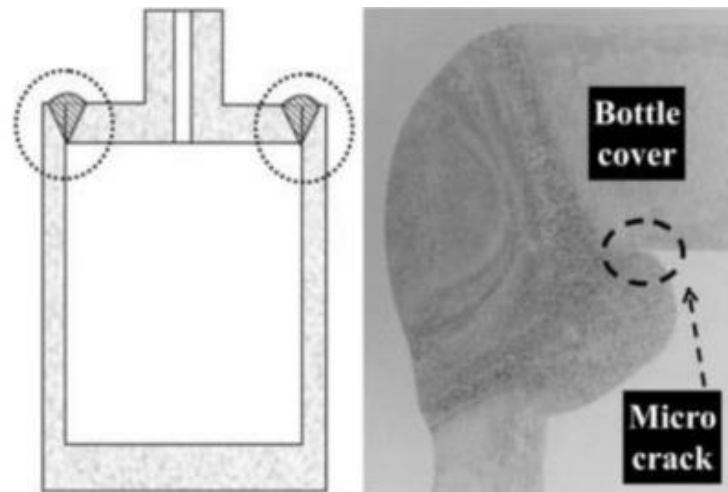


Figure 9: Susceptible locations for micro cracks of hydrogen storage tanks^[20]

Kamoutsi et. Al^[34] studied the corrosion-induced embrittlement of 2024 Al-alloy, doing a corrosion test according to ASTM G34-90 and they observed they observed the stages of corrosion. Except the observation of the corrosion stages, tensile tests were performed^[35]. So, the starting of corrosion in the material is pitting corrosion and after 2 to 4 hours starts the intergranular corrosion. It was observed exfoliation of grains on the surface and the creation of pathway from which corrosion can move in the material (Figure 10a). Also, distinct energy states trap hydrogen and these states are associated with varying microstructural trap which are activated at different temperatures. The trap's strength increases as the temperature rises. To 2024 Al-alloy were observed four traps as shown in Figure 10b.

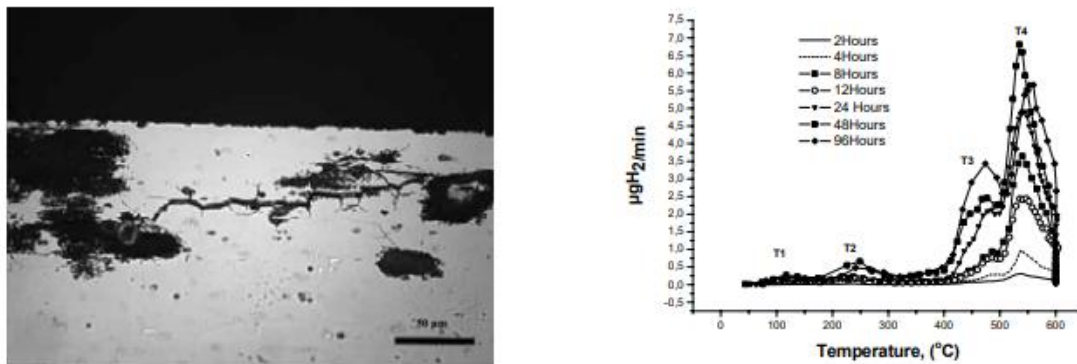


Figure 10: a) 2024 Al-alloy, intergranular corrosion leading to exfoliation, b) Microstructural traps activated at different temperatures^[20]

The dissolution of H₂ into the material can happen during heat treatments and during operation because of high temperatures. Despite H has low solubility in Al, the surface defects help H absorption. Grain Boundaries (GBs) are areas of increased vulnerability to electrochemical

attack, and they also allow for cracks to spread more easily throughout the microstructure of the alloy. Huan Zhao et al.^[9] studied a 7xxx Al-alloy with a composition of Al-6.22Zn-2.46Mg-2.13Cu-0.135Zr (wt.%) in its peak aged conditions (120°C for 24 hours). The electrochemical-charging of this alloy with H leads to a critical drop in the ductility compared with uncharged samples. In *Figure 10a* is shown the H desorption spectra in extended Data. The *Figures 10b-10c* highlight the microstructure across multiple length scales. In *Figures 10b-10c* is shown the role of GBs in the crack formation and propagation during deformation of H-charged material.

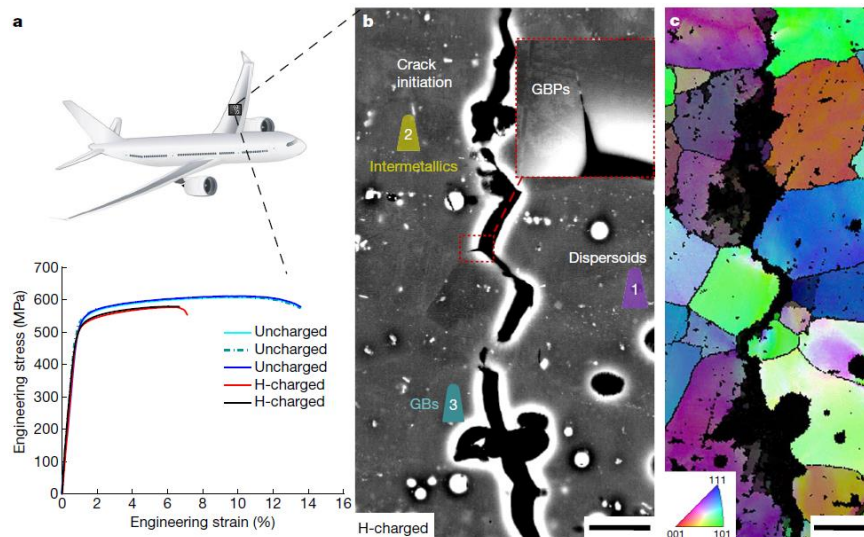


Figure 11: Microstructure of Al-Zn-Mg-Cu alloy, a) Stress-Strain curve of uncharged and H-charged samples in the peak-aged conditions (120°C for 24 hours), b) Backscattered electron imaging of an intergranular crack of the H-charged alloy subjected to tensile fracture, c) Electron backscatter diffraction imaging showing the crack along GBs^[9].

3.1. Models to Explain Hydrogen Embrittlement

In order to explain the Hydrogen Embrittlement of aluminum alloys have been listed many theories, HELP, HEDE, AIDE, HEMP and DHF. Hydrogen embrittlement is a complex phenomenon and requires to understand the interactions between hydrogen and metal surface, as well the enter and moving of hydrogen in the crystal lattice and its effects on crystal defects, precipitates and material's properties. The defects act as trap for hydrogen atoms. When the hydrogen is released from traps, it can cause fractures in previously cracked materials resulting in material's damage. The decreased solubility of hydrogen in aluminum alloys at lower temperatures can lead to the creation of cracks through the diffusion of hydrogen to defects and precipitates in aluminum alloys^[19].

3.1.1. Hydrogen Enhanced Local Plasticity Model

The Hydrogen Enhanced Local Plasticity Model (HELP) is the generally accepted theory for hydrogen embrittlement. According to this model, under constant load conditions, hydrogen diffuses into the material due to stress and continue to be gathered at the crack area. Once the concentration of hydrogen reaches a critical level, it will result to the formation of cracks in the

material. A study by Verners et al.^[21] on aluminum alloys with a Face-Centered Cubic (FCC) structure found that the microstructure influences the diffusivity of hydrogen. The presence of dislocations can increase the concentration of hydrogen and cause hydrogen embrittlement. Lynch's research also support the idea that HELP is the hydrogen embrittlement mechanism of FCC structured materials ^[20]. Gupta et al.^[22] used synchrotron microtomography to observe a 7075 Al-alloy sample after hydrogen charging and found that the hydrogen can cause the redistribution of hydrogen, forming an expansion and accumulation zone near intergranular cracks. The ability of hydrogen to easily become trapped in damaged areas is believed to cause the agglomeration of damaged areas, although it is not clear whether the agglomeration occurs before the development of intergranular cracks. In all images below (*Figure 11*) is shown by grey color the alloy matrix. In the matrix exist many dark objects, which are different types of microdamage and bright phases, which are intermetallic phases in 7075 Al-alloy, with different shapes. Other studies have shown that the presence of hydrogen can lead to a critical level of local plastic deformation at lower stress levels, resulting in the nucleation and development of cracks and eventually cause material failure^{[20],[23]}.

According to the HELP mechanism theory, the presence of hydrogen near the crack tip causes a decrease in the material's ability to resist dislocation movement through a reduction of the material's yield stress in the affected area, even at low levels of stress^[16].

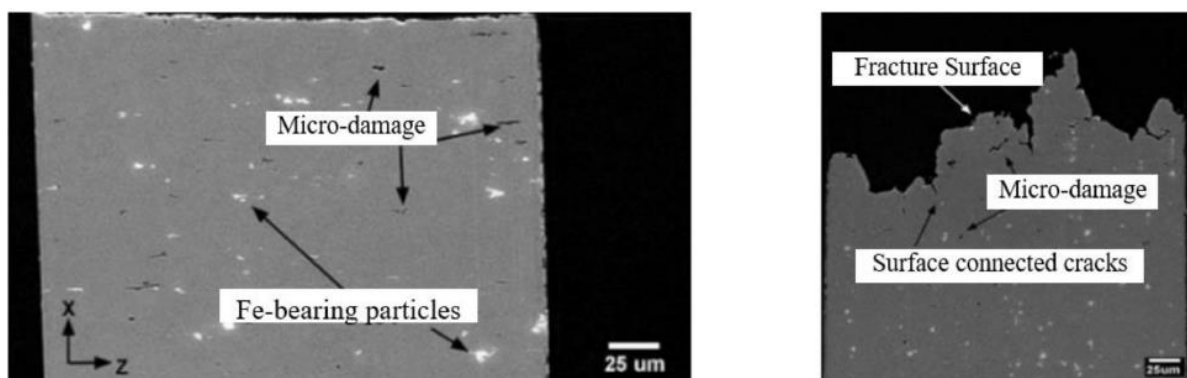


Figure 12: Synchrotron microtomography observation to Al- alloy sample after hydrogen charging^[20]

3.1.2. Hydrogen Enhanced Decohesion Mechanism

The Hydrogen Enhanced Decohesion Mechanism (HEDE) is a basic theory that explains the phenomenon of hydrogen embrittlement (HE). According to HEDE, hydrogen atoms decreases the cohesive strength of the material in the vicinity of a crack, when hydrogen atoms are present and exist stresses to the material, leading to fracture. This theory posits that lower local stress can cause damage to the bonds between atoms, resulting in the formation of microscopic cracks. However, this model is currently only theoretical and lacks experimental evidence^{[18],[20]}.

3.1.3. Hydrogen Pressure Theory

The presence of supersaturated hydrogen in an aluminum alloy can lead to the formation of micro cracks in the material in the form of H₂. The rise in hydrogen pressure occurs as the concentration of H₂ at these cracks increases. When this pressure is more than the yield stress of the material, the surface of the material swells and bubbles are created. This influences the

development of micro cracks and ultimately fracture. The presence of hydrogen enhances the movement of dislocations and concentrates them in high-stress areas, promoting ductile fractures at the cracks^[18].

3.1.4. Adsorption-Induced Dislocation Emission (AIDE)

A mechanism called AIDE is a combination of HELP and HEDE theory and shows that cracks form and grow due to the breakdown of cohesion and the release of dislocations at the crack. The combination of micro-void merging and slipping at the crack tip promote crack growth^[18]. The surface energy is impacted by the adsorption of hydrogen atoms on the metal surface, and these atoms either promote or limit the nucleation of dislocations on the surface^[20].

3.1.5. Hydrogen-Enhanced Strain-Induced Vacancy Generation (HESIV)

The vacancy formation energy is reduced because of the interaction between hydrogen and vacancies. This promotes the nucleation of the vacancy. So, the increased in vacancy density promotes the formation of H-vacancy complexes and leads to an enhanced pinning on mobile dislocations.

Some mechanisms, such as Hydrogen-induced micro-fracture mode (HAM), focus on the transition from ductile to brittle fracture in materials, others, such as hydrogen-enhanced macroscopic plasticity (HEMP), deal with the effects of hydrogen on the material's macroscopic plasticity when hydrogen is present in large amounts. Through hydrogen diffusion, the material softens and its yield strength decreases. Crack propagation and hydrogen embrittlement effects may be caused by one or a combination of these mechanisms. Because of the influence of the hydrogen, subcritical crack growth occurs in the material. To understand the crack initiation and the mechanisms that lead to crack propagation and failure in hydrogen embrittlement, both macro and microscale fractures need to be considered. When a material is under stress, hydrogen at the fracture tip decreases the cohesive strength of the material and causes it to fail. Additionally, if the tensile stress is more than the material's atomic strength at the fracture tip, hydrogen accumulates at the crack tip, weakening the cohesive strength and leading to subcritical crack propagation. The hydrogen atom then moves to a new crack position and cracking is propagating until the critical crack length is reached, causing the material's failure. The cracking growth is caused by dislocation motion at the fracture tip due to hydrogen atom buildup (HELP phenomenon)^[18].

3.2. Testing Methods and Measuring Techniques of Hydrogen Embrittlement

There are several methods for determining hydrogen embrittlement in material. These include the linearly increasing stress test (LIST), constant extension rate test (CERT), Slow strain rate testing (SSRT), temperature techniques desorption spectroscopy (TDS), permeation testing (PT), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

Linearly Increasing Stress Test (LIST) is a technique commonly used to estimate the influence of hydrogen embrittlement (HE) on materials. Two main procedures, Constant Load Test (CLT) and Constant Extension Test (CET), are used to determine the stress at which HE occurs.

However, other methods such as the Constant Extension Rate Test (CERT) and Slow Strain Rate Testing (SSRT) have also been employed to address the limitations of the LIST method. SSRT applies a constant progressive elongation to the specimen until it fails or fractures, but this method is time-consuming and can take a while to reach the threshold stress. CERT, on the other hand, relates the susceptibility of stress corrosion cracking (SCC) to the strain rate and provides data about the strain rate that is critical for SCC^[18]. HE is classified as a type of stress that does not affect the material unless it exceeds a certain stress value.

Thermal Desorption Spectroscopy (TDS) is a widely used technique for investigating hydrogen embrittlement and hydrogen-induced failure in materials, particularly steel. It allows for the determination and measurement of hydrogen diffused in the material. This is done by heating the sample under controlled conditions, which releases the hydrogen and allows for its quantification. TDS is a useful tool for understanding the role of hydrogen in failure mechanisms and the amount of diffusible hydrogen present in the material^[16].

Additionally, the Electrochemical Cathode Hydrogen Permeation method can analyze the presence of hydrogen embrittlement in the materials with a platinum wire mesh used as anode. Aluminum alloys are subjected to corrosive environments during their use, it is essential to conduct corrosion tests on these materials in such environments. After exposure to the corrosive environment, the samples are tested to detect the surface corrosion and to measure the mechanical properties (such as yield stress, ultimate stress, strain energy density etc.).^[20]

In order to evaluate a material's susceptibility to hydrogen embrittlement (HE), microstructural analysis plays a crucial role. Techniques such as Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) are commonly used to understand the internal structure of the material, as well as the impact of hydrogen on the microstructure.

3.3. Prevention of Hydrogen Embrittlement

To ensure safety, it is crucial to choose an appropriate prevention technique. Prevention methods can be divided into two categories: blocking hydrogen from the material by inhibiting film formation on the surface of aluminum alloys or using coating methods, and making the material more resistant to HE through heat treatment methods and refining grain methods. The following sections analyze some of the prevention methods of hydrogen embrittlement.

Finding ways to balance strength and HE resistance has proven to be challenging. Yuantao Xu et al.^[24] proposed a method of suppressing HE by introducing intermetallic compounds (IMCs) for hydrogen redistribution. 14 elements were added to a high-strength Al-Zn-Mg alloy to create a constant volume fraction of IMC particles. The results showed a correlation between hydrogen trapping energy from ab initio calculations and resistance to HE. Mn-rich Al₁₁Mn₃Zn₂ particles had the highest hydrogen trapping energy (0.859 eV/atom), reducing hydrogen occupancy in the η_2 (MgZn₂) phase interfaces and grain boundaries, the initiators of HE cracks. The addition of Mn did not harm the ductility and most Al₁₁Mn₃Zn₂ particles remained intact during deformation. The strong hydrogen trapping capacity of Al₁₁Mn₃Zn₂ prevented the localization of hydrogen-induced strain and initiation of HE cracks, preserving the ductility. This approach

effectively suppresses HE while retaining ductility and can guide the design of high-strength metallic alloys that are tolerant to HE

3.3.1. Film forming Method in Alkaline Environment

One method to prevent hydrogen embrittlement in aluminum alloys is to create a protective film on the surface of the material. The study by Dey et al. [25] investigated the creation of surface films on 7075 aluminum alloy to improve resistance to hydrogen embrittlement. They done slow strain rate tests on the alloy in both NaOH and NaCl solutions. The results showed that the NaOH-treated material had a stronger influence in preventing HE during the hydrogen charging process. This happened because to the NaCl-treated material the OH⁻ content was low. They discovered that the protective film on the surface of the alloy was an oxide rich in Zn and Mg. They also noted that the composition of the alloy 7175 is similar to that of 7075, suggesting that similar treatment could also be applied to achieve hydrogen embrittlement resistance, but this has not been confirmed by experiments.

3.3.2. Acid Radical Suppression

The compound dichromate exhibits potent adsorption and oxidation characteristics and it can be used to treat aluminum materials. Rocca et al. [26] found that treating the materials with acid radical solutions and observing them via SEM showed that acid radicals can repair defects in the surface film and create a stable, corrosion-resistant film. They also found that treating the materials with a Cr₂O₇⁻² containing solution resulted in a smoother surface without defects, while a MoO₄⁻² containing solution has some defect areas.

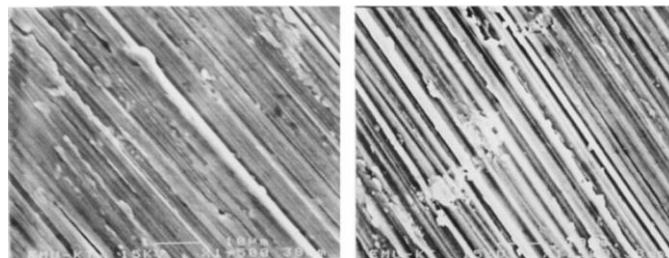


Figure 13: Surface of samples in a)Cr₂O₇⁻², b)MoO₄⁻² treatment^[20]

The presence of chromium in the passivation film generated by dichromate treatment enhanced its ability to inhibit hydrogen embrittlement.

3.3.3. Sodium Silicate Solution Inhibition Method

It was observed that using gas tungsten arc welding (GTAW) to join the 7075 Al-alloy bottle cap to the bottle body causes issues such as hydrogen embrittlement. This was caused by hydrogen penetrating microcracks and it was proposed to cover the surface of the welding zone with sodium silicate solution and limiting the depth of hydrogen penetration.^[20]

3.3.4. Cadmium, Nickel and other Coatings

A film is applied to the liner to improve its performance during hydrogen's storage tank production. Hillier proposed the use of zinc and nickel alloys and found that hydrogen penetration in steel can be reduced by using the following methods. By adding nickel on the material, a film forms and is used as a limit to hydrogen, because the diffusion coefficient of hydrogen in nickel is very low ($1.2 \cdot 10^{-10} \text{m}^2 \text{s}^{-1}$). The ability of hydrogen to pass through the coating is based on its diffusion rate through the coating. In some cases, hydrogen atoms combine to form molecules before entering the coating and then escape and form bubbles. Cadmium can also be used to recombine hydrogen in the coating and reduce its entry.

The use of coated metal to prevent HE is a very common method. Some materials, such as Pt, Cu and Ni are used as protective film, because they create a thin film to the surface of the aluminum alloy, which reduces the diffusion of hydrogen in the material. Gold, tin and certain tin-lead alloy coatings can act as limit to hydrogen diffusion in the material.

3.3.5. Metal Oxide for Coating

The compact nature of the aluminum oxide film makes it effective at preventing hydrogen penetration. Efforts have also been made to optimize the technology used to deposit the film.

3.3.6. Nitride as Coating

The density and uniformity during filling makes nitrides to be effective limits against hydrogen penetration. In the research of Melendez et al. ^[27], it was revealed that a $1 \mu\text{m}$ thick TiN coating on a 0.35mm thick stainless steel specimen exhibited exceptional barrier properties. Meanwhile, Bazzanella et al. ^[28] investigated the effect of aluminum in TiN coatings and observed that it readily forms compounds with oxygen, thereby impeding Ti oxidation. Although this technique has been recommended for use on high-strength steel, it could be potentially extended to aluminum alloys, though it needs experimental certification.

3.3.7. Heat Treatment of Materials

Wu et al. ^[29] studied the hydrogen embrittlement (HE) sensitivity of GCr15 bearing steel using two heat treatment methods: quenching and tempering (QT) and pre-quenching and austenite tempering (PQA). The findings indicated that the PQA-treated samples displayed greater mechanical stability and resistance to HE, as demonstrated by hydrogen bubble experiments and indentation tests. Differences in diffusion coefficients and the number of hydrogen capture sites were also found between the QT and PQA-treated samples. Another study by Song et al. ^[30] was identified that 7175 Al-alloy demonstrates two peak aging states during aging at 413-443K, with the second peak aging state exhibiting high strength and better HE resistance compared with the first peak aging state aged at 413K. Additionally, it was discovered that heat treatment can alter the size and distribution of precipitated phases in the grains, thereby limiting HE and enhancing the mechanical properties and HE resistance of the alloy.

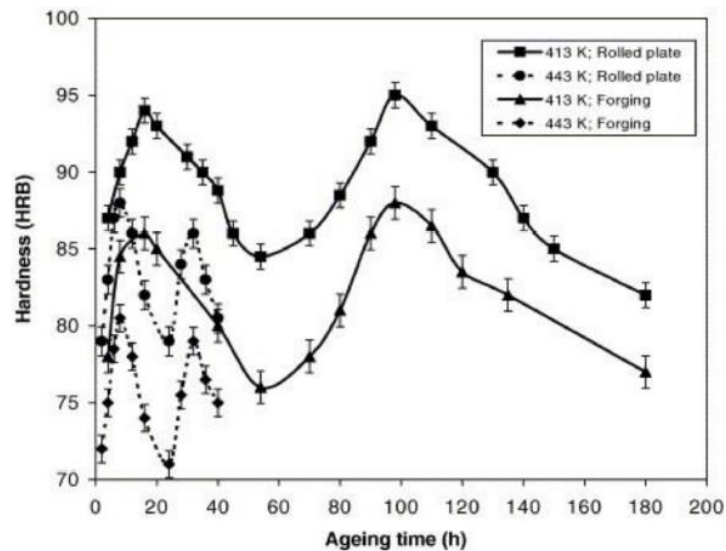


Figure 14: Peak points of 7175 Al-alloy aging at 413-443K

3.3.8. Grain Refining

It has been proved through experiments that vibrating a sample results in reduction in the size of crystallized crystals. The size of the crystal grains influences the susceptibility of the material to hydrogen embrittlement (HE), with smaller crystal grains associated with reduced HE sensitivity. Park et al.^[31] performed tensile tests on hydrogen-charged samples and through SEM observation they analyzed the fracture surfaces of both hydrogen-free and charged samples. The samples without hydrogen displayed ductile fracture surfaces with well-formed pits (irrespective of the grain size). Fracture surfaces with ductile characteristics were detected even at the edge of the sample when the grain size was less than $20\mu\text{m}$. Conversely, only the central portion of the sample exhibited ductile fracture surfaces when the grain size was larger than $20\mu\text{m}$. Moreover, the hydrogen atoms exhibit greater activity in coarse grains, and that refining the grain structure can prevent the transition from ductility to brittleness in steel, thereby limiting HE. In addition, the research demonstrated that grain refinement can decrease the hydrogen diffusion coefficient of the material.

3.4. New high-strength alloys with resistance to hydrogen embrittlement

There are several new alloys that have been developed for hydrogen storage with improved strength and resistance to hydrogen embrittlement. These materials can be a promising solution for hydrogen embrittlement and to increase strength, but they are still under development and more research is needed to optimize their properties and to make them more cost-effective. Some examples of materials include:

1. *Magnesium-based alloys*: Magnesium alloys have a high hydrogen storage capacity and are lightweight, making them a potential candidate for hydrogen storage. However, magnesium alloys are also susceptible to hydrogen embrittlement. Researchers have been working on developing magnesium alloys with improved resistance to hydrogen embrittlement.

One approach to improve the resistance to hydrogen embrittlement in Magnesium alloys is to add elements such as zinc, yttrium and rare earth elements. These elements can form stable hydrides and reduce the amount of free hydrogen in the alloy, which can help to reduce hydrogen embrittlement.

One example is the development of magnesium-lithium alloys, which have been found to have improved resistance to hydrogen embrittlement. It was found that the addition of lithium to magnesium can improve the resistance to hydrogen embrittlement by forming a stable lithium hydride phase. Another example is the use of magnesium-zirconium alloys, which have been found to have improved resistance to hydrogen embrittlement by forming a stable zirconium hydride phase.

Another approach is to use microstructural design to improve the resistance to hydrogen embrittlement. Researchers have been exploring the use of nanocomposites and multilayer structures in magnesium alloys to improve the resistance to hydrogen embrittlement.

2. *Titanium-based alloys*: Titanium alloys have a high strength-to-weight ratio and are resistant to hydrogen embrittlement. However, hydrogen can still cause some degree of embrittlement in titanium alloys.

One approach to improve the resistance to hydrogen embrittlement in Titanium alloys is to add elements such as palladium, nickel and molybdenum. These elements can form stable hydrides and reduce the amount of free hydrogen in the alloy, which can help to reduce hydrogen embrittlement.

One example is the development of titanium-palladium alloys, which have been found to have improved resistance to hydrogen embrittlement. It was found that the addition of palladium to titanium can improve the resistance to hydrogen embrittlement by forming a stable palladium hydride phase. Another example is the use of titanium-nickel alloys, which have been found to have improved resistance to hydrogen embrittlement by forming a stable nickel hydride phase.

Another approach is to use microstructural design to improve the resistance to hydrogen embrittlement. Researchers have been exploring the use of nanocomposites and multilayer structures in titanium alloys to improve the resistance to hydrogen embrittlement.

It is worth noting that titanium-based alloys are still under development and more research is needed to optimize their properties and to make them more cost-effective for hydrogen storage applications. Additionally, the hydrogen storage capacity of titanium based alloys is relatively low compared to other materials like magnesium and metal hydrides.

3. *Nickel-based alloys*: Nickel-based alloys such as Inconel and Hastelloy have excellent corrosion resistance and high strength. However, they are also susceptible to hydrogen embrittlement.

One approach to improve the resistance to hydrogen embrittlement in Nickel alloys is to add elements such as molybdenum, chromium and tungsten. These elements can form stable

hydrides and reduce the amount of free hydrogen in the alloy, which can help to reduce hydrogen embrittlement.

One example is the use of Inconel 718 alloy, which have been found to have improved resistance to hydrogen embrittlement. Inconel 718 alloy is a nickel-chromium-molybdenum alloy that has been designed to resist hydrogen embrittlement by having high levels of nickel and molybdenum. Another example is the use of Hastelloy X alloy, which have been found to have improved resistance to hydrogen embrittlement. Hastelloy X alloy is a nickel-chromium-molybdenum alloy that has been designed to resist hydrogen embrittlement by having high levels of chromium and molybdenum.

Another approach is to use microstructural design to improve the resistance to hydrogen embrittlement. Researchers have been exploring the use of nanocomposites and multilayer structures in nickel alloys to improve the resistance to hydrogen embrittlement.

4. *Metal Hydrides*: Metal hydrides are materials that can store hydrogen within their crystal structure. They are made of a metal and a hydrogen-containing compound. However, some metal hydrides can be also susceptible to hydrogen embrittlement under certain conditions.

One approach to improve the resistance to hydrogen embrittlement in metal hydrides is to use composites of metal hydrides with other materials, such as carbon or silicon, which can help to reduce the amount of free hydrogen in the material and thus reduce hydrogen embrittlement.

One example is the use of LaNi₅-based alloys, which have been found to have improved resistance to hydrogen embrittlement. LaNi₅ is a metal hydride that can store hydrogen in its crystal structure and it is less susceptible to hydrogen embrittlement than other metal hydrides. Another example is the use of TiFe-based alloys, which have been found to have improved resistance to hydrogen embrittlement. TiFe is a metal hydride that can store hydrogen in its crystal structure and it is less susceptible to hydrogen embrittlement than other metal hydrides.

Another approach is to use microstructural design to improve the resistance to hydrogen embrittlement. Researchers have been exploring the use of nanocomposites and multilayer structures in metal hydrides to improve the resistance to hydrogen embrittlement.

It is important to notice that metal hydrides are still under development and more research is needed to optimize their properties and to make them more cost-effective for hydrogen applications. Additionally, the cyclability of metal hydrides is relatively low compared to other materials and this is a challenge that needs to be addressed.

5. *Carbon-based materials*: Carbon-based materials like carbon nanotubes and graphene have been studied for their potential use in hydrogen storage because of their high surface and high thermal conductivity. However, these materials are also susceptible to hydrogen embrittlement under certain conditions.

One approach to improve the resistance to hydrogen embrittlement in carbon-based materials is to use composites of carbon-based materials with other materials, such as metal hydrides or

metal-organic frameworks (MOFs), which can help to reduce the amount of free hydrogen in the material and thus reduce hydrogen embrittlement.

One example is the use of carbon nanotubes (CNTs) reinforced metal hydrides composites, which have been found to have improved resistance to hydrogen embrittlement. It was found that the addition of CNTs to metal hydrides can improve the resistance to hydrogen embrittlement by reducing the amount of free hydrogen in the material. Another example is the use of metal-organic frameworks (MOFs) reinforced graphene composites, which have been found to have improved resistance to hydrogen embrittlement. It was found that the addition of MOFs to graphene can improve the resistance of to hydrogen embrittlement by reducing the amount of free hydrogen in the metal.

Another approach is to use microstructural design to improve the resistance to hydrogen embrittlement. Researchers have been exploring the use of nanocomposites and multilayer structures in carbon-based materials to improve the resistance to hydrogen embrittlement.

It is important to note that carbon-based materials are still under development and more research is needed to optimize their properties and to make them more cost-effective for hydrogen storage applications. Additionally, the hydrogen storage capacity of carbon-based materials is relatively low compared to other materials like hydrides and magnesium.

4. Conclusion

Transportation plays a crucial role in worldwide energy consumption, largely due to the use of internal combustion engines. The usage of fossil fuels has resulted in environmental deterioration and energy deficiencies, inspiring researchers to look for sustainable alternatives. Hydrogen presents a hopeful solution as it boasts high energy density, exceptional efficiency and emits no greenhouse gases when utilized as fuel. Its implementation in the automotive sector, which currently depends mainly on gasoline, could have a substantial effect.

The storage of hydrogen is a crucial aspect for the global implementation of hydrogen as a fuel for vehicles. Hydrogen can be stored in compressed H₂ tanks, liquid H₂ tanks, cry-compressed tanks or with chemical ways (Sorbents, Metal Hydrides, Chemical Hydrides). The ideal pressure for on-board hydrogen systems in vehicles is typically between 35 to 70MPa. Hydrogen can be stored in four types of pressure vessels, which can be cylindrical, polymorph, or toroidal in shape. These include metallic pressure tanks (Type I), pressure tanks made up of a cylindrical metallic liner hoop that is reinforced with a fiber resin composite wrap (Type II), and pressure vessels made entirely of composite materials such as a metallic or plastic liner wrapped in carbon fibers in a polymer matrix (Type III and Type IV, respectively). Presently, the Type III composite storage tank, featuring an aluminum inner liner, is the most widely adopted hydrogen tank.

The material of the tank is a critical factor in the storage of compressed hydrogen. Some properties that are required to be met for H₂ tanks are: safety, high storage density, durability, corrosion resistance and low weight. The tank should withstand the operational and external stresses and the operational conditions should not affect the material and structure of the tank.

Aluminum is a material that meets these requirements due to its various beneficial properties and it is suitable for use in hydrogen storage tanks. The most important factor of using aluminum in the automotive industry is its light weight and durability. The high strength-to-weight ratio of aluminum makes it an ideal choice for reducing the weight of vehicles, which is a key goal in the industry in order to meet stricter emissions targets. Also, Aluminum has a high level of formability, which means that it can be easily shaped and worked into different shapes, such as cylindrical or spherical tanks. It is also resistant to corrosion, which makes it a durable material to work with.

Aluminum alloys are suitable materials for hydrogen storing tanks, specifically the Al-Cu alloys-2xxx, the Al-Mg alloys-5xxx, the Al-Mg-Si alloys-6xxx, the Al-Zn alloys-7xxx and Al-Li alloys include materials that are used in hydrogen storage tanks because of their properties. *The 2xxx Al-alloys* are Aluminum-Copper alloys and they are heat treatable. They have high strength, high performance and they have a great variety of applications due to their excellent strength over a wide range of temperatures. *The 5xxx Al-alloys* are Aluminum-Magnesium alloys and they are non-heat treatable. They have the highest strength of the non-heat treatable alloys. *The 6xxx Al-alloys* are Aluminum-Silicon-Magnesium alloys and they are heat treatable. The addition of Magnesium and Silicon to Aluminum creates a compound of Magnesium-Silicide which allows the material to be solution heat treated for improved strength. *The 7xxx Al-alloys* are Aluminum-Zinc alloys and they are heat treatable. These alloys are known for their strength and they have a great variety of applications because of their high strength-to-weight. The strength of these alloys is attained through the formation of a large number of nanosized precipitates during an aging thermal treatment. *Al-Li (Aluminum-Lithium) alloys* are a group of light-weight metal alloys composed of aluminum and lithium. By using Al-Li alloys in metal components, a 20% reduction in weight is expected. They have high strength, low density, and improved corrosion resistance. Al-Li alloys also have a higher elastic modulus, lower thermal expansion, and better stiffness compared to conventional aluminum alloys. Although Al-Li alloys display resistance to fatigue crack propagation, their corrosion resistance can be improved.

Some specific examples of alloys that are used for hydrogen tanks are:

- 5052 Al-alloy which has high strength ($\sigma_{UTS}=270\text{MPa}$) and high fatigue strength.
- 5083 Al-alloy which has high strength ($\sigma_{UTS}=315\text{MPa}$).
- 6061 Al-alloy which is known for its strong lightweight properties. The hardness and strength are determined by the precipitate type, density and size ($\sigma_{UTS}=310\text{MPa}$).
- 7075 Al-alloy: this alloy boasts remarkable mechanical properties and boasts toughness, high strength, good ductility and resistance to fatigue ($\sigma_{UTS}=270\text{MPa}$). Despite being more prone to embrittlement due to microsegregation compared to other Al-alloys, it still has excellent corrosion resistance.

There are technical difficulties in the widespread use of hydrogen, including the absence of safe, leakage and interaction between hydrogen and material's tank. A phenomenon that is observed to H₂ tanks is the Hydrogen Embrittlement. Hydrogen diffuses into many metals and causes undesired effects. Hydrogen can interact with the crystal lattice of some materials (such

as iron, steel, nickel, titanium, vanadium, zirconium, silicon) that are used in pressure vessel design. The diffusion of hydrogen into materials can result in hydrogen embrittlement, stress corrosion cracking, hydrogen-induced cracking, and other adverse effects, which may lead to fracture and failure of the material. The presence of hydrogen atoms can cause localized plastic deformation and increase the rate of crack propagation in the metal, elevating the danger of sudden failure of high-pressure hydrogen tanks. Hydrogen embrittlement affects material's mechanical properties, including the fracture toughness, strength, fatigue strength and/or ductility. The ability of a metal to react, deform, or elongate under stress is limited due to the metallurgical interaction between the atomic hydrogen and the material's structure. As a result, the material can turn "brittle" under stress, leading to fracture at a much lower strain or stress level than expected.

In order to explain the Hydrogen Embrittlement of aluminum alloys have been proposed many theories, HELP, HEDE, AIDE, HEMP and DHF. Hydrogen embrittlement is a complex phenomenon and requires to understand the interactions between hydrogen and metal surface, as well the enter and moving of hydrogen in the crystal lattice and its effects on crystal defects, precipitates and material's properties. The defects (which include vacancies, dislocations, grain boundaries) act as trap for hydrogen atoms. When the hydrogen is released from traps, it can cause fractures in previously cracked materials resulting in material's damage. The decreased solubility of hydrogen in aluminum alloys at lower temperatures can lead to the creation of cracks through the diffusion of hydrogen to defects and precipitates in aluminum alloys.

There are several methods for determining hydrogen embrittlement in material. These include the linearly increasing stress test (LIST), constant extension rate test (CERT), Slow strain rate testing (SSRT), temperature techniques desorption spectroscopy (TDS), permeation testing (PT), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

To ensure safety, it is crucial to choose an appropriate prevention technique. Prevention methods can be divided into two categories: blocking hydrogen from the material by inhibiting film formation on the surface of aluminum alloys or using coating methods, and making the material more resistant to HE through heat treatment methods and refining grain methods.

Except the methods to prevent hydrogen embrittlement, there are several new alloys that have been developed for hydrogen storage with improved strength and resistance to hydrogen embrittlement. These materials can be a promising solution for hydrogen embrittlement and to increase strength, but they are still under development and more research is needed to optimize their properties and to make them more cost-effective. Some examples of materials include:

- i. Magnesium-based alloys
- ii. Titanium-based alloys
- iii. Nickel-based alloys
- iv. Metal Hydrides
- v. Carbon-based materials

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