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FINAL REPORT

ENERGY DENSE, LIGHTWEIGHT, DURABLE, SYSTEMS FOR STORAGE AND DELIVERY OF HYDROGEN

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Chapter 1

INTRODUCTION

1.1 Background

The Hydrogen Posture Plan prepared by the U.S. Department of Energy's (DOE's) Office of Energy Efficiency and Renewable Energy (EERE) emphasizes the use of hydrogen as an alternative energy carrier that can enhance long-term energy security while mitigating the effects of air pollution and greenhouse gas emissions. Hydrogen is envisioned as a flexible, safe, affordable and domestic energy source that can be utilized in all sectors of the economy and all regions of the country (*USDOE, 2004*). However, broad commercial use of hydrogen fuel as an energy carrier requires major development efforts in several segments of the hydrogen economy, including production, delivery, storage, conversion, and end-use (*USDOE, 2002*).

Safe and efficient storage of hydrogen, either during transportation or use, either in stationary or portable applications, is a key enabling technology for the advancement of the hydrogen economy. For example, the Hydrogen Storage Program element of the DOE's technical plan focuses on developing and verifying viable on-board hydrogen storage systems that by the year 2010 can achieve energy density levels of 2 kW-hr/kg (6% capacity by weight) for storage in the solid state, or 1.5 kW-hr/L for storage in the liquid state, at a cost of \$4/kW-hr. By the year 2015, the energy density levels for hydrogen storage are expected to rise to 3 kW-hr/kg (9% capacity by weight) for storage in the solid state, or to 2.7 kW-hr/L for storage in the liquid state, at a reduced cost of \$2/kW-hr (*USDOE, 2004*).

Two major approaches are being presently pursued for reaching the hydrogen storage goals of DOE's Posture Plan:

In the near term, the development of advanced concepts for conformability and cost reduction of storage tanks for hydrogen in the form of either compressed gas, or cryogenic liquid; and

In the long term, the development of reversible solid-state hydrogen storage materials, as well as new materials and design concepts for light-weight, safe and durable hydrogen storage tanks with high energy density.

Currently, hydrogen is stored in both off-board tanks and on-board prototype vehicles as a high-pressure compressed gas or a cryogenic liquid. Compressed hydrogen gas tanks are likely to be used in early hydrogen-powered vehicles, but they have to meet affordable cost and efficient packaging requirements to expedite the transition to a

commercially viable hydrogen economy. Furthermore, tanks for storing hydrogen in solid-state, as a liquid chemical, or other forms in the future, will have to conform to strict space limitations, as well as meet special performance requirements, such as safe and effective heat management during fueling.

Table 1-1 Targets for on-board hydrogen storage system.

Storage Parameter	Units	2007	2010	2015	Gasoline (current)
System Gravimetric Capacity:					
Specific-energy from H ₂	kWh/kg	1.5	2	3	3.5
Net useful energy/max system mass	kg H ₂ /kg system	0.045	0.06	0.09	
System Gravimetric Capacity:					
Specific-energy from H ₂	kWh/L	1.2	1.5	2.7	2.5
Net useful energy/max system volume	kg H ₂ /L system	0.036	0.045	0.081	
Storage System Cost	\$/kWh net	6	4	2	1.30
Fuel Cost	\$/kg H ₂	200	133	67	-
	\$/gge at pump	-	2-3	2-3	-
Durability/Operability	°C				
Operating ambient temperature	°C	-20/50	-30/50	-40/60	
Min/max delivery temperature	Cycles	-30/85	-40/85	-40/85	
Cycle life (1/4 tank to full)	% of mean	500	1000	1500	
Cycle life variation	(min) at % confidence	N/A	90	99	
Min delivery pressure from tank	Atm (abs)	FC: 8 ICE: 10	FC: 4 ICE: 35	FC: 3 ICE: 35	
Max delivery pressure from tank	Atm (abs)	100	100	100	
Charging/Discharging Rates					
System fill time (for 5 kg)	min	10	3	2.5	2-5
Minimum full flow rate	(g/s)/kW	0.02	0.02	0.02	
Start time to full flow (20 °C)	s	15	5	5	
Start time to full flow (-20 °C)	s	30	15	15	
Transient Response 10%-90% and 90%-0%	s	1.75	0.75	0.75	
Fuel Purity (H ₂ from storage)	%H ₂ (dry basis)	99.99	99.99	99.99	

Another approach relies on storing hydrogen in solid-state by employing metal hydrides. This technique utilizes chemical bonds between hydrogen and metal atoms to store hydrogen within the metal alloys. The advantage of this technology lies in the ability to store hydrogen in a low pressure setting, alleviating the need for compression. Storing hydrogen in a solid-state form requires cryogenic temperatures (-253°C). Such low temperatures are a major disadvantage to solid -state storage solutions for several reasons.

- (1) Significant amounts of energy are needed to liquefy hydrogen and sustain a stable solid state over a prolonged period of time.
- (2) The energy loss from cryogenic temperature boil off is significant, therefore making the technology inefficient.

- (3) The average consumer will not be able to operate the equipment necessary to store solid state hydrogen on-board a vehicle.
- (4) The typical heat of reaction for metal hydrides can reach levels of 30 to 40 kJ/mol. This implies that large amounts of energy need to be rejected during refueling, thus increasing refueling time and cost beyond acceptable levels (*Young, 2006*).

In this study, we will focus on the development of lightweight storage systems as a short term goal for hydrogen storage.

1.2 System Requirements

Guidelines for the system requirements of an on-board hydrogen storage system have been outlined by the U.S. Department of Energy in conjunction with industry. Such requirements were set in the form of targets for calendar years 2007, 2010 and 2015. The requirements account for a complete system to achieve a 300-mile vehicle driving range. A complete system is defined by all of the components used to make hydrogen a useable fuel source; this includes but is not limited to, the tank, valves, regulators, piping, mounting, insulation, etc. A complete summary of the DOE's hydrogen storage targets is presented in Table 1.1.

Chapter 2

CURRENT RESEARCH EFFORTS ON LIGHTWEIGHT STORAGE TANKS

2.1 Introduction

Hydrogen (H_2) is an element that poses many important properties for the development of a non-oil based fuel economy. Hydrogen is the most simple of all elements but its energy content is the highest per unit weight of any known fuel (52,000 Btu/pound). Hydrogen energy content per unit weight is three times that of gasoline. However, the energy content per unit volume is approximately four times lower than that of gasoline due to the low density of hydrogen.

Hydrogen properties related to storage systems and utilization as an energy source are listed in Table 2.1. These properties are to be considered in design applications and for determining system requirements for storing applications.

Table 2-1 Hydrogen properties.

Property	Value
Melting Point *	$T_m = -259.34\text{ }^{\circ}\text{C}$
Boiling Point *	$T_b = -252.87\text{ }^{\circ}\text{C}$
Density of Gas*	$\rho_g = 0.08987\text{ kg/m}^3$
Density of Liquid*	$\rho_l = 70.99\text{ kg/m}^3$
Flammability Concentration in Air	4.1 % – 72.5 %
Autoignition Temperature	$T_{ai} = 530\text{ }^{\circ}\text{C}$
Higher Heating Value (HHV)	HHV = 141.79 MJ/kg = 39.39 kWh/kg
Lower Heating Value (LHV)	LHV = 119.96 MJ/kg = 33.39 kWh/kg

A gram of hydrogen gas occupies about 11 liters (2.9 gallons) of space at atmospheric pressure. Thus, for storage or delivery the gas must be intensely pressurized to several hundred atmospheres and contained in a pressure vessel. In liquid form, hydrogen can only be stored under cryogenic temperatures (*Becker, 2001*). Therefore, the great challenge for future generations of hydrogen-powered vehicles is to develop strong, safe, but lightweight storage systems with conformable tank shapes that can be adapted easily to different vehicle structures.

Comprehensive research activities have been recently initiated by the U.S. DOE to develop lightweight composite tanks for storing hydrogen in the form of compressed gas. Currently, DOE's research and development for physical hydrogen storage is focused on the development of high-pressure (10,000 psi) composite tanks, cryo-compressed tanks, conformable tanks and other advanced concepts for storing hydrogen as compressed gas on-board vehicles. DOE is also investigating both compressed hydrogen and liquefied hydrogen storage systems for off-board storage at hydrogen fueling stations.

2.2 Compressed Hydrogen

Hydrogen can be compressed and stored in high-pressure tanks, but this process requires significant energy consumption. The compressed gas has to occupy a very large volume, which results in low energy density storage when compared to a traditional gasoline tank. A hydrogen gas tank that stores an amount of energy equivalent to that of a gasoline tank would have to be more than 3,000 times larger than the gasoline tank. It was also reported that when compressing hydrogen gas into high-pressure tanks, each additional cubic foot of hydrogen gas compressed into the same space would raise the required pressure level by another atmosphere of pressure, i.e. by 14.7 psi. Nowadays, high-pressure tanks can achieve maximum internal pressures of about 6,000 psi, and therefore, they must be periodically tested and inspected to ensure their safe utilization (*FuelCellStore.com*, 2003).

To achieve a fully functioning hydrogen economy, hydrogen needs to be stored in a wide range of application scenarios, involving various scales, operational and environmental conditions. The easiest way of storing hydrogen at the present time is in the form of pressurized gas. According to the United Kingdom Hydrogen Energy Network (H2NET), the two typical configurations that are currently used for storing hydrogen as a compressed gas are described in Table 2.2 (*H2NET*, 2004).

Table 2-2 Typical configurations of storage tanks for compressed hydrogen.

Configuration	Advantages	Disadvantages
Steel alloy cylinders at 200 bars (R & D devices now up to pressures of 700 bar).	Simple Indefinite storage time No purity limits	Hydrogen embitterment Danger of auto ignition if ruptured
Composite reinforced plastic tank with max. internal pressure capability of 300 bar	Simple Indefinite storage time No purity limits Good burst behavior (rips apart rather than disintegrating).	Danger of auto ignition if ruptured

Modern containers are constructed of novel composite materials that have the potential to lead to significant weight reductions. Gas pressures of up to 300 bars (4,350 psi) are used in current zero-emission vehicle prototypes. Nevertheless, these containers have to occupy large volumes in order to store significant levels of energy, and therefore, their applications are usually limited to large vehicles, such as busses or vans (Dornheim, 2006).

2.2.1 *Quantum Trishield Hydrogen Storage Systems*

Quantum Fuel Systems Technologies Worldwide, Inc (QFSTW) started a research program sponsored by USDOE and Lawrence Livermore National Laboratory to develop ultra lightweight, low-cost hydrogen storage tanks (*Sirosh, 2002*). Quantum developed carbon fiber-reinforced 5000-psi and 10,000-psi compressed hydrogen storage cylinders as an alternative that would be compatible with the cost expectations of the automotive industry, and also meet safety standards. The inner liner of the tank is a high molecular weight polymer that serves as a hydrogen gas permeation barrier. A carbon fiber-epoxy resin composite shell is placed over the liner and constitutes the gas pressure load-bearing component of the tank. Finally, an outer shell is placed on the tank for impact and damage resistance. The pressure regulator for the 10,000-psi (70 MPa) tank is located in the interior of the tank (*Ko et al., 2004, 2005*). Such tanks were close to meeting the 2007 targets for weight, energy density, and specific energy of 6% hydrogen by weight. However, they utilized premium aerospace-grade carbon fiber reinforcement to satisfy the structural requirement of supporting 23,500 psi burst pressure. Therefore, they could not achieve the cost goal of \$5 per kW-h, since the reported cost was \$10-\$17 per kW-h (*Able, 2006*). Low-cost, commercial grade carbon fibers were employed to fabricate 10,000-psi storage tanks for compressed hydrogen with the same level of performance as tanks fabricated from high-cost, aerospace grade carbon fibers (*Ko et al., 2005*). Although such tanks can yield a specific energy density of approximately 1.3 kW-hr/kg, further design improvements are necessary, most likely through unconventional means, to exceed this value (*Dubno, 2007*).

The researchers of QFSTW also demonstrated that the use of active sensors to monitor the health of the storage system might be an attractive and safe approach for integrated design of hydrogen storage tanks. Their results showed that for each tank design considered in the study, the strain signature of a damaged tank deviates from its initial strain signature, when the tank was in a healthy condition. Thus, if a sufficiently economical and robust sensor array can be mounted on a tank to monitor continuously the status of its entire health, then such an instrumentation system would enable weight and cost reductions while also acting as an active safety feature.

2.2.2 *MAGNA STYR*

As an independent engineering and manufacturing partner to automakers located in Graz, Austria, MAGNA STYR has partnered with Mercedes-Benz, Chrysler, SAAB, BMW and others to provide solutions to engineering applications within the automotive industries.

MAGNA STYR coordinated an Integrated Project named “StorHy”, as part of the European initiative, driven by major European car manufacturers, on automobile hydrogen storage (*Struble, 2004*). This initiative covers the full spectrum of currently qualified technologies. The project aims at developing robust, safe and efficient on-board hydrogen storage systems suitable for use in hydrogen-fueled fuel cells or internal combustion engines. The project addresses the compressed gas, cryogenic and solid hydrogen storage applications (*Struble, 2006*).

In the compressed gas initiative, MAGA STYR conducted research work to develop a lightweight compressed hydrogen vessel capable of storing hydrogen gas at a nominal pressure of 700 bar (10,000 psi), along with the necessary peripheral equipment. The main characteristics of the desired tank are summarized as follows (*Strubel, 2006*):

- At 20°C, the pressure of 700 bars corresponds to a volumetric energy density greater than 1.4 kWh/liter.
- At this pressure, a 125 liter reservoir (inner volume) can store approximately 5 kg of hydrogen so that ranges of 420-500 km driving autonomy per filling can be achieved with a car equipped with a typical ~70 kWe fuel cell.
- The tank has to achieve gravimetric energy density larger than 2.2 kWh/kg. Since the calorific power of hydrogen is 33.33 kWh/kg, the corresponding targeted hydrogen storage capacity (system mass fraction) is about 6 wt%.
- The tank has to withstand operating temperatures between –40°C and +85°C, and the overall hydrogen permeation/leak rate of the tank should be maintained below 1 cm³/hr per tank-liter in order to meet the ISO TC 197 standard and the TRANS/WP29/GPRE/2004/3 regulations.

In this context, more than 50 liner systems were developed and analyzed during the first two years to address the issues of hydrogen permeation and chemical compatibility during compressed gas storage. Two different composite systems were developed and investigated for high pressure storage of hydrogen:

- The first system is based on a thermoset resin wet winding process on thermoplastic liners or metallic liners, with special emphasis on tank manufacturing and the development of a processing technology for high volume production. Both 6 liter and 34 liter, 700 bar tank prototypes were manufactured and characterized for design validation and cycling behavior.
- The second system is a thermoplastic-based modular multi-cylinder storage system, with special emphasis on continuous cylinder production, dome production and joining. The feasibility of manufacturing composite tubes with thermoplastic matrix material in combination with reinforcement fibers and a thermoplastic liner has been successfully demonstrated. The device for thermoforming the cylindrical section to the metallic end-caps has been already set up. The first tanks based on this system were manufactured and tested; the results obtained will contribute to the optimization of the process (*Strubel, 2007*).

The results indicated that such developed 700-bar tanks can achieve gravimetric densities about 5 wt% and volumetric and 0.6 kWk/liter. Preliminary cost analysis indicated that large scale production of such tanks will cost about 400 euros per each kilogram of the stored hydrogen.

2.2.3 *Honda FCX*

Honda demonstrated the use of compressed hydrogen tanks in its new fuel cell vehicle FCX (*Honda, 2008*). The vehicle utilizes a high-pressure hydrogen tank that is made of an aluminum liner wrapped with carbon fibers. The fuel capacity of this tank is 3.75 kg of hydrogen with an internal pressure of 34.5 MPa (5,000 psi). The FCX brochure, shown in Appendix I, indicates that the tank is cylindrical in shape with oblate end caps. Sarkar and Banerjee (2005) assumed that the liner thickness is 0.241 cm at the cylindrical parts and thickens by factor of 3.5 at the domes of the end caps. As a result, the tank mass was estimated to be 56.91 kg, i.e. can achieve gravimetric density of about 6.6 wt%. They also estimated that the net energy required to produce and compress 1 kg of hydrogen in such a tank is 202 MJ/kg.

2.2.4 *Daimler Chrysler F-Cell Vehicle*

The F-cell vehicle has been built by Daimler Chrysler based on the Mercedes-Benz A-class technology (*Daimler Chrysler, 2006*). This test vehicle was built under near production conditions. The entire fuel system cell system is located in the sandwich construction floor, which kept the interior space of the car the same. The system utilized two cylindrical hydrogen tanks of maximum pressure of 350 bar (5,000 psi). It is reported that the performance of this vehicle is comparable to that of an internal combustion engine vehicle. In 2007, the company Daimler Research and Development team started testing the new B-Class F-Cell in Sweden. In this version, the pressure in the hydrogen tank was doubled from 350 to 700 bars, which boosted the vehicle's driving range to 400 kilometers (*Daimler Chrysler, 2008*).

2.3 *Cryogenic Storage*

The main advantage of cryogenic storage is that it requires quite a low working pressure compared to the high pressure storage system necessary for gaseous hydrogen. Another potential advantage of cryogenic storage is a considerable reduction of weight by using new composite materials, with which a specific energy storage mass similar to a conventional fuel tank can be achieved.

Liquid hydrogen occupies a relatively small volume. Furthermore, this method is distinguished by the highest weight-related capacity for hydrogen storage. However, hydrogen has to be cooled down to -253°C, i.e. 20K, in order to be liquefied, which

consumes about one third of its energy content. The tanks have a costly but effective insulation: the thickness of the shell is about 3 centimeters, which corresponds to about 3 meters of styrofoam. Nevertheless, a small amount of hydrogen (about 1-3% per day) is lost continuously due to warming and evaporation (Dornheim, 2006).

Krainz *et al.* (2003) developed state-of-the-art, double-wall cylindrical tanks for passenger vehicles, capable to hold a hydrogen storage mass of up to 10 kg. The shell of the tank was made of stainless steel due to its resistance against hydrogen brittleness and its negligible hydrogen permeation. The weight of the whole tank system, including valves and heat exchanger, exceeded 100 kg. The space between the inner and outer shells was used for thermal insulation purposes. Several layers of foils and high vacuums of 10^{-3} Pa were used to reduce heat entry. A support structure made of materials of low thermal conductivity, such as glass or carbon fiber reinforced plastics, was used to keep the inner tank in place. Due to the high production costs of the above configurations, new concepts of lightweight hydrogen storage tanks are under investigation (Krainz *et al.*, 2004).

Aceves et al. (2005) of Lawrence Livermore National Laboratory have undertaken the following tasks to design and build high performance hydrogen storage containers:

- Developed three conceptual design configurations for conformable containers manufactured through filament winding of continuous fiber composites, and utilized finite element analyses to identify an optimum geometry. A detailed design and experimental pressure testing of these containers is currently ongoing.
- Built and tested a container for cryogenic liquid hydrogen, which can achieve the high packaging density of liquid nitrogen (LN₂) without the evaporative losses typical of liquid hydrogen (LH₂) containers. This container was tested in a pickup truck, which was refueled several times with both compressed and liquid hydrogen, thus demonstrating its flexible fueling capability. A new generation of this container is currently under design to meet the DOE's 2010 weight target and the 2007 volume target for hydrogen storage tanks.
- Built the first macrolattice conformable container. This cubic container was constructed with polycarbonate struts, held together with metallic struts. A prototype of the container was pressure tested to 170 psi. The strut arrangement can also provide heat transfer paths for the efficient thermal management of hydrogen storage materials. This container design promises optimum utilization of available space in a vehicle.
- Analyzed and tested the innovative approach of storing hydrogen in liquid nitrogen, which is based on the fact that hydrogen can be absorbed in various fluids, such as liquid nitrogen.

2.4 Summary on Critical Elements in Hydrogen Storage

The on-going studies have addressed the possibilities of successfully storing hydrogen in three different media, or states:

- (1) Liquefied hydrogen
- (2) Compressed hydrogen gas, and
- (3) Hydrogen storage materials.

Liquefying hydrogen is an expensive process, which consumes large amounts of energy due to the requirement of attaining and preserving cryogenic temperatures. A major challenge is the development of advanced insulation procedures to reduce fuel loss by boil-off effects. However, high values of hydrogen energy density can be reached through this approach.

Compressed hydrogen gas is a more simple approach than liquefying hydrogen, because it only requires the containment of gas at high-pressure levels. A pressure vessel capable of containing high -pressure gas is required for this type of storage medium in order to attain practical levels of energy density storage. The amount of hydrogen that can be stored in a vessel is dependent upon the pressure level and the volume of the vessel. For example, 5 kg of hydrogen can be stored in a 390 liter tank at a pressure of 20 MPa. By increasing the pressure to 35 MPa, the volume required to store 5 kg of hydrogen is reduced to 250 liter.

Hydrogen storage materials use the metallic properties of various alloys to store hydrogen in their atomic microstructure. A heat exchanger is used to charge and discharge the hydrogen from the storing alloy. The weight and size of the heat exchanger, as well as other requirements, have to be accounted for when considering the development of such a system.

The tanks that are presently used for on-board hydrogen storage are designed for either cryogenic liquid hydrogen or for hydrogen in the gas-state, compressed at pressures of either 5,000 or 10,000-psi. Such tanks have been certified worldwide and have been demonstrated in several prototype fuel cell vehicles. All-composite tanks designed for an internal pressure of 10,000 psi have demonstrated a factor of safety of 2.35 (23,500-psi burst pressure), as required by the European Integrated Hydrogen Project specifications as well as by the US Department of Energy.

The review of the current state-of-the-art in the this area indicates that on-board compressed hydrogen storage systems that contain enough hydrogen to provide driving distances equivalent to those of conventional vehicles are too bulky, thus compromising passenger and cargo space. Extensive research is still needed at the stage of materials development, since none of the current hydrogen storage systems meets the combined gravimetric, volumetric, and cost targets for either 2010 or 2015. Although energy density levels as high as 5% capacity by weight have been already reached, the targets of 6% capacity by weight for 2010 and 9% capacity by weight for 2015 pose tough technical challenges, since they address system-level capacities that include the materials, the tank, and all the various components needed for the storage system. Two major barriers must be overcome in the foreseeable future in order to achieve these targets:

- **Materials**: High-pressure containment limits the choice of construction materials and fabrication techniques within the weight, volume, performance, and cost constraints associated with hydrogen storage tanks for broad commercial applications. Research on new materials such as metal, ceramic or polymer matrix composites, improved resins and engineered fibers is critical for meeting cost targets without compromising performance. Development of such advanced materials would be beneficial for both on-board and off-board storage, as well as for the delivery of hydrogen, either through pipes or by trucks.
- **Lack of Tank Performance Data**: At the present time, no comprehensive data base and no reliable knowledge is available to enable thorough understanding of the fundamental mechanisms that govern the service life cycle of hydrogen storage tanks made of composite materials. Real-life data are needed on the performance of such tanks in likely operating scenarios, as well as on their possible failure modes and criteria, in order to design their structure for optimal tradeoffs between performance and cost.

Chapter 3

PRELIMINARY ON-BOARD STORAGE TANKS DESIGN

3.1 Introduction

The design and development of a hydrogen storage vessel is governed by size, weight, and hydrogen storage capacity. Several criteria must be met to store hydrogen on-board a vehicle and successfully provide a fuel source to meet the standard 300-mile driving range. All the lightweight designs devised and evaluated at this stage of the research project are focused on compressed hydrogen gas storage. The primary objective is to efficiently design a compressed gas storage vessel to achieve a minimal volume while attaining a maximum storage pressure level. As several other studies have shown, the implementation of advanced composite materials is essential to withstand the high tensile hoop stresses associated with containing a high- pressure gas without significant weight penalties.

Several criteria, as listed below, must be addressed in order to achieve the above objective:

- (1) High pressure containment
- (2) Minimization of tank volume
- (3) Lightweight design
- (4) Hydrogen containment
- (5) Thermal insulation
- (6) Heat exchange system and configuration
- (7) Optimization

The research conducted has been aimed mainly at the first and the second of above criteria. The design goal is to achieve a level of 10,000 psi (70 MPa) of internal pressure, while optimizing the tradeoffs between the maximum pressure and the volume capacity of the tank.

3.2 Preliminary Analysis

Closed form calculations were performed to determine the internal forces within the walls of a cylindrical pressure vessel with spherical end caps when a 10,000 psi (70 MPa) internal pressure is applied. The tank was assumed to have an inner radius of 6 inches and the length of the cylindrical part is 22.5 inch in order to accommodate a capacity of 15 gallons (3,450 in³) of the hydrogen. The axial force per unit length (P_z) and the hoop force per unit length (P_x), shown in Figure 3.1, were calculated for pressure vessels made of composite materials with three different types of fibers: Fiberglass, Kevlar, and Carbon Fiber. The minimum wall thickness of each pressure vessel was calculated for a factor of safety of 2.35.

Figure 3-1 Internal forces in an axisymmetric shell.

The following equations from the thin-wall pressure vessel theory were used to determine the internal stresses in the pressure vessel, σ_h and σ_a . The corresponding results are presented in Table 3-1. Because of the symmetry around the longitudinal axis, the resultant force has only a component along the longitudinal z-axis, defined in terms of the internal pressure p by:

$$P_z = p \pi r^2 \quad (3.1)$$

In the tangential direction, the resultant force can be calculated by

$$Q = pL(2r) \quad (3.2)$$

By satisfying the equilibrium of the forces in the z-direction, the axial tensile stress in the vessel wall σ_a can be calculated by:

$$\sigma_a = \frac{P(\pi r^2)}{2\pi r t} = \frac{pr}{2t} \quad (3.3)$$

The hoop stresses σ_h can also be calculated by satisfying the equilibrium condition in that direction as:

$$\sigma_a = \frac{P(2rL)}{2rt} = \frac{pr}{t} \quad (3.4)$$

A composite laminate with a combination of 0-degree, 90-degree, and ± 45 -degree layers was used to build the vessel walls to the minimum thickness values listed in Table 3-1. The 0-degree and 90-degree layers represent 90% of the overall laminate thickness, and their role is to provide the necessary stiffness and strength levels in the axial and hoop directions. The reinforcement layers with ± 45 -degree fiber orientations form 10% of the overall thickness of the wall, and they are included to provide shear stiffness and strength, as well as to provide additional integrity to the vessel structure. The values of the tensile strengths of this laminate were determined and reported as F_{at} and F_{ht} as in Table 3-1.

Table 3-1 Preliminary design of composite storage tanks for compressed hydrogen gas.

<i>Material</i>	<i>Vessel Dimensions</i>		<i>Pressure</i>	<i>Resultant Forces</i>		F_{at}	F_{ht}	<i>Thickness</i>	
	<i>Length</i>	<i>Radius</i>		F_h	F_a			F_h	F_a
	[in]	[in]	[psi]	[lb/in]	[lb/in]	[psi]	[psi]	[in]	[in]
E-glass	22.50	4.95	10,000	49,500	24,750	46,702	84,411	1.32	1.19
Kevlar	22.50	4.95	10,000	49,500	24,750	59,465	58,450	1.91	0.94
Carbon fiber	22.50	4.95	10,000	49,500	24,750	120,000	124,000	0.90	0.46
E-glass	45.00	9.90	10,000	99,000	49,500	46,702	84,411	2.64	2.38
Kevlar	45.00	9.90	10,000	99,000	49,500	59,465	58,450	3.81	1.87
Carbon fiber	45.00	9.90	10,000	99,000	49,500	79,770	82,526	2.70	1.40

Table 3-1 and equations (3) and (4) verify that the primary concern for a pressure vessel design is the hoop force per unit length, F_h , since the magnitude of the force F_h is half the magnitude of F_a . Therefore, the required thickness in the circular or hoop direction is twice that of the wall thickness required in the longitudinal direction. The results of Table 3-1 show that carbon is the best candidate based on the minimal wall thickness of the tank. This is because it requires the minimal overall wall thickness in both the axial and hoop directions. The ability to tailor the lay-up of composite material configurations offers the possibility of using less material in the axial direction and more material in the hoop direction to attain the strength required to ultimately withstand the internal forces associated with the high internal pressure of compressed hydrogen gas.

3.3 Finite Element Analysis

The results listed in Table 3.1 provide preliminary designs for the lay-up configurations of hydrogen storage vessels made of composite materials, which can be further expanded by using finite element analysis. The ANSYS finite element software was used to model two pressure vessels with different lay-up configurations:

- (1) All- composite pressure vessel based on Carbon fibers.
- (2) Hybrid pressure vessel based on Aluminum liner over wrapped with Carbon fiber reinforcement, which is guided by the basic requirements of the Department of Transportation (DOT-CFFC, 2007). It should be noted here that this design concept is the most common today in the pressure vessels industry; however the DOT specifications require that the maximum service pressure in such vessels not to exceed 350 MPa (5,000 psi).

A uniform internal pressure of 10,000 psi (70 MPa) was applied to each vessel. For both configurations, the The finite element analysis was used to determine the maximum deformation and stress levels in the pressurized vessel. The main input parameters, both material and geometric characteristics, as well as the corresponding results are summarized below.

3.3.1 *Pressure vessel made of Carbon fibers*

Configuration 1:

Material: Carbon Fiber/Epoxy

Fiber orientations: 0/90/ $\pm$ 45 degree

Lay-up composition by percentages of fiber orientations: 45%/45%/10% Layer thickness: 0.23 mm (0.009 in.)

Number of Layers: 100

Total wall thickness: 23 mm (0.9 in.)

In this configuration, it is assumed that an equal number of 0-degree and 90-degree layers are used, each fiber orientation forming a fraction of 45% of the overall wall thickness, whereas the $\pm$ 45- degree layers form 10% of the overall wall thickness. Figure 3.2 illustrates by colored fringe patterns the Von Mises equivalent stress and the displacement fields generated in the vessel wall by an applied internal pressure of 10,000 psi. A uniform stress field with a value of 42.77 ksi (30 MPa) was calculated on the outer wall surface of the vessel, while an equivalent Von Mises stress of 62.77 ksi was calculated on the inner surface of the vessel. This indicates that a pressure vessel of such design configuration behaves as a thick shell, which brings up the approximate nature of the preliminary calculations used to predict the results shown in Table 3-1.

(a) Axial Displacement

(b) Von Mises Equivalent Stress on Outer Surface

(c) Carbon Fiber Orientation

(d) Von Mises Equivalent Stress on Inner Surface

Figure 3-2 Displacement and Stress plots, and sketch of lay-up configuration for the carbon fiber pressure vessel with 45% of 0° plies, 45% of 90° plies and 10% of ±45° plies.

Configuration 2:

Material: Carbon Fiber/Epoxy

Fiber orientations: 0/90/±45 degrees

Lay-up composition by percentage of fiber orientations: 30%/60%/10%

Layer thickness: 0.23 mm (0.009 in.)

Number of Layers: 100

Total wall thickness: 23 mm (0.9 in.)

In this configuration, it is assumed that 30% of the carbon fibers are oriented at 0-degree and 60% are oriented at 90-degrees, thus providing further reinforcements in the hoop direction, in which the maximum stresses are expected to develop. Figure 3.3 depicts the distributions of the stress and displacement fields generated in the vessel wall by an applied internal pressure of 10,000 psi (70 MPa). No significant change was observed in

the stress field from that developed in Configuration 1. However, about 34 percent reduction in the axial displacement was noticed when using the lay-up Configuration 2, which uses fewer fibers in the axial direction. As more stiffening occurs in the hoop direction due to the increase of the amount of fibers, the Poisson's effect yields smaller deformation in the axial direction

Figure 3-3 Displacement and stress plots, and sketch of lay-up configuration for the carbon fiber pressure vessel with 30% of 0° plies, 60% of 90° plies and 10% of ±45° plies.

3.3.2 Aluminum pressure vessel reinforced with Carbon fibers

In this design, Carbon fiber plies were wrapped around a 0.54-inch thick aluminum cylinder that has the same internal radius of 4.95 inches as the all-Carbon fiber vessel analyzed previously. Furthermore, two different lay-up configurations of the Carbon fiber plies were examined by using 3D finite element modeling as in the previous design. The applied internal pressure was also kept the same at 10,000 psi (70 MPa).

Configuration 1:

Material: Aluminum vessel reinforced with a carbon fiber/epoxy composite shell

Aluminum thickness: 14 mm (0.54 in.)

Fiber orientations: 0/90/ $\pm$ 45 degrees

Lay-up composition by percentages of fiber orientations: 45%/45%/10%

Layer thickness: 0.23 mm (0.009 in.)

Number of Layers: 40

Total wall thickness of the hybrid tank: 23 mm (0.9 in)

(a) Axial Displacement

(b) Von Mises Equivalent Stress on Outer Surface

(c) Carbon Fiber Orientation

(d) Von Mises Equivalent Stress on Inner Surface

Figure 3-4 Displacement and stress plots, and sketch of lay-up configuration for the Al. pressure vessel reinforced with carbon fibers at 45% of 0° plies, 45% of 90° plies, 10% of $\pm$ 45° plies.

Figure 3-4 illustrates the fringe patterns of the Von-Misses equivalent stresses and axial displacements developed in this configuration as the internal pressure of 10,000 psi is applied. The maximum stress was calculated at the inner surface of the shell and it is

equal to 71.75 ksi (1.5% less than that developed in the all- carbon fiber vessel). However, due to the thick aluminum core, this design was much stiffer than the all-carbon vessel, which is evident from the smaller axial displacement field shown in Figure 3-4(a).

Configuration 2:

(a) Axial Displacement

(b) Von Mises Equivalent Stress on Outer Surface

(c) Carbon Fiber Orientation

(d) Von Mises Equivalent Stress on Inner Surface

Figure 3-5 Displacement and stress plots, and sketch of lay-up configuration for the Al. pressure vessel reinforced with carbon fibers at 30% of 0° plies, 60% of 90° plies and 10% of ±45° plies.

Material: Aluminum vessel reinforced with a Carbon fiber/epoxy composite shell

Aluminum thickness: 0.54 in.

Fiber orientations: 0/90/±45 degrees

Lay-up composition by percentage of fiber orientations: 30%/60%/10%

Layer thickness: 0.009 in.

Number of Layers: 40

Total wall thickness of the hybrid tank: 0.9 in.

In this configuration, it is assumed that 30% of the carbon fiber reinforcements are oriented at 0-degree and 60% are oriented at 90-degree. Figure 3-5 depicts the distributions of the Von Mises stress and axial displacement fields generated in the vessel wall by an applied internal pressure of 10,000 psi (70 MPa). No significant change was observed in the stress field from that developed in Configuration 1. However, about 8 percent reduction in the axial displacement was noticed when using the lay-up Configuration 2. Thus, this configuration provides a stiffer pressure vessel.

3.4 Results and Discussion

The process of the pressure vessel design started with closed form solutions to determine the internal forces developed when the tank is loaded by a uniform internal pressure of 10,000 psi (70 MPa). Subsequently, the minimum wall thickness that is required to withstand the internal forces and maintain a 2.25 factor of safety was calculated for three different candidate fiber materials. This required thickness was then used in four different finite element models to closely examine the detailed state of stress developed in the vessel wall by the applied internal pressure of 10,000 psi. The finite element models consisted of an all-carbon fiber design and an aluminum vessel reinforced with layers of carbon fiber. The overall wall thickness of each model was held constant. The lay-up configurations were altered to examine the effects of different relative percentages of the 0°/90°/45° layers. The 30%/60%/10 % configuration was found to be beneficial in reducing the maximum axial displacements for both design configurations. The 3D finite element models captured the through-thickness stress distribution, which could be expected due to the relatively thick walls of the vessels considered in this analysis. Table 3.2 summarizes the maximum values of Von Mises stresses and axial displacements calculated for each design configuration.

Table 3-2 Maximum stress and displacement values calculated through 3-D FEA.

	<i>Maximum Displacement</i> [in]	<i>Maximum Stress</i> [ksi]
All-Carbon Fiber 45%/45%/10%	0.1765	62.7
All-Carbon Fiber 30%/60%/10%	0.1172	62.7
Carbon Fiber / reinforced Al. 45%/45%/10%	0.0627	71.7
Carbon Fiber / reinforced Al. 45%/45%/10%	0.05765	71.7

For the all-Carbon fiber design, a 34% reduction in the axial displacement was attained when changing the lay-up from the 45/45/10% composition to the 30/60/10% configuration. An 8 % reduction in displacement was achieved for the Aluminum vessel reinforced with Carbon fiber as a result of the same change in the lay-up configuration, from the 45/45/10% composition to the 30/60/10% composition. This indicates that the 30/60/10% lay-up is beneficial in increasing the stiffness of such pressure vessels.

Equivalent Von-Mises stress distributions were obtained from the finite element analysis. These results were used in a failure analysis based on the Von-Mises failure criterion to determine the factor of safety for each design. The resulting factor-of-safety values are listed in Table 3.3. It is necessary to remember that a 2.25 factor of safety value was incorporated into the preliminary calculations of the minimum wall thickness required to withstand the internal forces F_h and F_a associated with an applied internal pressure of 10,000 psi. The values of the safety factors resulting from the finite element models are about 2.0, which is less than 2.25, most likely due to the fact that the through-the-thickness variations of the Von Mises stresses are considered in the finite element analysis, whereas a uniform through-the-thickness stress distribution is assumed in the closed form solution. Additionally, it should be remembered that the closed form solution is based on the hoop and axial stress components not the Von-Mises stress, which is utilized in the FE analysis.

Table 3-3 Results of carbon fiber failure analysis based on the von Mises failure criterion.

<i>Design</i>	<i>Strength Parameter</i>	<i>Carbon Strength Values</i> [ksi]	<i>Corresponding Stress Values</i> [ksi]	<i>Factor of Safety</i>	<i>Vessel Weight</i> [lbs]
All-Carbon Fiber	F_{ht}	124	62.7	1.98	28
	F_{ht}	124	62.7	1.98	28
Aluminum reinforced with Carbon fibers	F_y	68	71.7	0.95	62.4
	F_y	68	71.7	0.95	62.4

The results shown in Table 3.3 indicate that:

- The benefits of adopting an integrated material-structure approach to achieve weight savings in the design of high pressure tanks for storing gaseous hydrogen are illustrated by the above results, mostly in terms of the higher factors of safety associated with the all-Carbon tanks, as compared to the Carbon –reinforced Aluminum tanks.
- The benefits of tailoring the geometry and material design to the specific loading environment of hydrogen tanks are evident from the changes in the value of the safety factor as the lay-up orientation or composition changes.
- The aluminum core is not suitable for lightweight design of hydrogen tanks, since it does not reduce the stress levels developed on the inner wall surface of the pressure vessel. Therefore, hydrogen tanks ought to be built entirely of composite layers based on carbon fibers or other innovative composite materials.

Additionally, the presence of the aluminum at the inner surface will make the aluminum always subjected to the maximum stress due to an internal pressure. Although the aluminum can sustain such stress at pressures in the magnitude of 5,000 psi, the results in Table 3.3 indicates that it will fail under pressures of 10,000 psi or higher.

3.5 Hydrogen Storage Capacity

The calculation of the weight and volume of the storage hydrogen tank involves the determination of the compressibility factor for the hydrogen gas, z , as a function of internal pressure (*Jones and Dugan, 1996; Takeichi, 2003; Dogan, 2006*). The values compressibility factor of the hydrogen gas at 298 °K (77 °F) to calculated the hydrogen storage performance as a function of the internal pressure are given in Table 3.6 (*Takeichi, 2003*). The weight of the compressed hydrogen gas is calculated using Equation 3.5.

$$W_{H_2} = \frac{MPV_i}{zRT} \quad (3.5)$$

where: M is the molar mass of the Hydrogen = 2.016 lbm/lbmol
 P is the internal pressure in the pressure vessel,
 V internal volume of the tank = 2,240 in³
 R is the universal gas constant = 1,545.3 ft.lbf/lbmol.R
 T is the hydrogen gas temperature inside the tank, Rankines

Figure 3-6 Values of compressibility factor of the Hydrogen gas at 77 °F.

Substituting the above values into Equation 3.5 yield the weight of stored compressed hydrogen in the tank is 3.06 lb. As a result, the design configurations shown above would result in a specific energy densities of 10% for All-carbon fiber vessel and 4.88% for the aluminum reinforced with carbon fiber vessel.

Chapter 4

ALTERNATIVE DESIGN CONFIGURATIONS WITH NON- TRADITIONAL GEOMETRIES

4.1 Introduction

The preliminary design of on-board hydrogen storage tanks presented in Chapter three as well as the design configurations found in the available literature are based upon utilizing a cylindrical tank with two end caps as shown in Figures 3.1 thru 3.5. One of the major problems with this design configuration is high weight of the storage tank due to the high pressure capability required. As a result, such tanks could not meet the DOE energy density requirements presented in Table 1.1. Another problem is the large tank size, which reduces the available space in the vehicle trunk (*Neira and Scudelari, 2005*). These challenges motivated the development of new storage tanks with unconventional geometries. Such new design configurations are expected to provide more conformability since they can fit easily in any tight space.

Initial designs for a hydrogen storage system utilized closed-form solutions to attain the internal forces developed due to high pressure levels. From attainment of the internal forces, the required material thickness to withstand these forces was determined. With the thickness requirements attained, finite element analysis was used to compare the use carbon fiber and aluminum design and a homogenous carbon fiber configuration as presented in Chapter Three. Acknowledging the basic engineering principles that internal stresses are half in magnitude for a spherical tank as opposed to cylindrical tank designs, the focus of tank configuration moved to address the spherical concepts.

4.2 Spherical versus Cylindrical Design Configurations

A shape optimization was performed to analyze various spherical and cylindrical tank configurations. Table 4.1 presents a sample of the results generated during this process. Therefore, a multi-spherical approach which combines spheres to attain a single volume of 15 gallons of hydrogen under an internal pressure of 10,000 psi (700 bar) is pursued to address the issue of practical on-board storage applications as well as the higher stress levels attained in cylindrical tanks.

The factors for introducing a spherical hydrogen storage concept are based on basic engineering principles that state the derived stress is a function of the pressure, radius, and thickness. Spherical tanks were shown to have much less stress than that in cylindrical vessels of the same volume. Such a reduction in stress due only to the change in geometry is a significant increase and is beneficial because:

- A stress reduction by a geometry change only will increase the amount of pressure sustained inside the vessel and ultimately increase the amount of hydrogen stored per volume.
- Stress reductions will decrease the thickness dimension required to achieve a particular factor of safety in a direct comparison to a cylindrical design. Minimal thickness will reduce the cost per storage system by limiting the usage of high performance materials i.e. carbon fiber.
- Options to vary the spherical dimensions will utilize free space on-board a standard vehicle. Various sizes of spherical tanks can be dimensioned to allowable free space inside a vehicle frame, chassis, cargo areas, etc.
- Several small spherical tanks will address the pressure drop inside a tank as the fuel is depleted. Maintaining several smaller storage systems as seen in Figure 4.1 (b) will minimize the pressure drop as fuel is used as opposed to single storage tank or various larger storage systems.

(a) 6-sphere design with merged connections

(b) Multiple sphere design without merged connections

Figure 4-1 Multiple spherical tank designs.

Table 4-1 Weight and energy efficiency of different design configuration of a Hydrogen Tank that stands 10,000 PSI.

Shape and Dimensions	Hydrogen Storage	Material	Max Tensile Force (lb/in)	Allowable Stress (Psi)	Wall Thickness (in.)	Tank Weight (lbs)	Energy Density, wt %
12 x 12 x 34.5 in.	$V=3,450 \text{ in}^3$ Hydrogen weight = 7.07 lb	E-Glass	90,000	84,411	1.60	222.68	5
		Kevlar 49	90,000	58,450	2.31	200.12	5
		C-Fiber	90,000	82,526	1.64	164.60	6
19 x 19 x 19 in.	$V=3,457 \text{ in}^3$ Hydrogen weight = 7.09 lb	E-Glass	70,350	84,411	0.52	90.33	12
		Kevlar 49	70,350	58,450	0.76	78.55	13
		C-Fiber	70,350	82,526	0.54	66.65	16
13 x 13 x 39 in.	$V=3,451 \text{ in}^3$ Hydrogen weight = 7.08 lb	E-Glass	48,750	84,411	0.58	90.59	12
		Kevlar 49	48,750	58,450	0.83	78.77	13
		C-Fiber	48,750	82,526	0.59	66.84	16
13 x 13 x 39 in.	$V=3,441 \text{ in}^3$ Hydrogen weight = 7.06 lb	E-Glass	44,250	84,411	0.46	90.64	12
		Kevlar 49	44,250	58,450	0.66	78.81	13
		C-Fiber	44,250	82,526	0.47	66.88	16
24 x 24 x 12 in.	$V=3,435 \text{ in}^3$ Hydrogen weight = 7.05 lb	E-Glass	33,750	84,411	0.40	90.18	12
		Kevlar 49	33,750	58,450	0.58	78.41	13
		C- Fiber	33,750	82,526	0.41	66.54	16

4.3 Finite Element Analysis of Hydrogen Tanks

The general finite element package ADINA was used to generate a set of finite element models for hydrogen tanks of spherical and cylindrical configurations to investigate the state of stress that develops in the tank wall and optimize the wall thickness. All models were built using four-node shell elements as shown in Figure 4.2. The tank wall was assumed to be carbon fiber/epoxy composite, whose strength in the tensile direction of the composite is 85 ksi. Although this value for the composite strength seems to be very conservative, it matches the strength that we obtained from the material testing that was performed on coupon level testing during prototyping as it will be described in Chapter Five of this report.

Spherical tanks of internal diameters of 18.8 in. (15-gallon tank) and 13 inch (5-gallon tank) were modeled. Different thicknesses were assumed for each model and the stresses were calculated under the effect of an internal burst pressure of 23,000 psi. As the service pressure expected in these tanks is 10,000 psi, a factor of safety of 2.3 is kept the same for all designs.

Figure 4-2 Finite element models of spherical and cylindrical tanks.

Figure 4-3 illustrates by fringes the stress distribution in the tank wall due to an internal pressure of 23,000 psi. Noticeable are the stress concentration zones that developed around the neck vicinity in Figures 4-3 (a), (c) and (d). Such regions constitute the main zone for potential tank failure.

Figure 4-3 Stresses in 15-gallon spherical tanks, thickness 1.4 in.

The effect of wall thickness on the state of stress developed in the tank wall is investigated. Tables 4-2 and 4-3 illustrate the change of the maximum values of various stress components due to reducing the tank wall thickness in a 9-inch and 13-inch diameter spherical tanks respectively.

Table 4-2 Effect of varying the wall thickness on critical stress in 9-inch diameter spherical tank due to a burst pressure of 23,000 psi.

<i>Thickness</i> [in]	<i>Stress-11</i>	<i>Stress-12</i>	<i>Stress-13</i>	<i>Stress-22</i>	<i>Stress-23</i>	<i>Stress-33</i>
1.0	59,136	128,310	127,650	137,706	31,593	145,084
0.9	65,254	139,625	138,596	140,250	34,641	143,617
0.8	72,819	151,447	150,021	147,599	38,418	147,888
0.7	81,922	143,965	143,488	157,929	49,346	159,630
0.6	Model Failed due to Large Pressure					

Table 4-3 Effect of varying the wall thickness on critical stress in 13-inch diameter spherical tank due to a burst pressure of 23,000 psi.

<i>Thickness</i> [in]	<i>Stress-11</i>	<i>Stress-12</i>	<i>Stress-13</i>	<i>Stress-22</i>	<i>Stress-23</i>	<i>Stress-33</i>
2.0	36236	244017	244155	154721	40026	156678
1.9	38235	254445	254685	159126	40762	162790
1.8	40540	257687	257597	155148	47135	161106
1.7	43320	255714	256959	154225	55467	159401
1.6	46735	240142	242075	155268	58363	160476
1.5	51463	213059	213832	156916	63473	162318
1.4	Model Failed due to Large Pressure

Figure 4-4 Stress distribution in cylindrical tanks under 23,000 psi.

(a) Shear Stress τ_{yz}

(b) Shear Stress τ_{xz}

(c) Shear Stress τ_{xy}

Figure 4-5 Shear Stress Distribution in Cylindrical Tanks under 23,000 psi.

In a similar way, a 3D finite element model was developed for a cylindrical tank with a 12-inch diameter and the length of the cylindrical part is 22 inches. The inlet has a length of 1.5 inch and its diameter is 2 inches. The radius of the fillet between the inlet and the dome is 1 inch. The tank wall is assumed to be built of 100 layers of carbon fibers. The thickness of each layer is 0.009 inch, thus a total wall thickness is 0.9 inch. The fiber orientation is $30^\circ/60^\circ/\pm 45^\circ$ with orientation percentages of 45%/45%/10%. The stress components were calculated under the effect of an internal burst pressure of 23,000 psi. Figure 4-5 illustrates by fringes the shear stress components developed in the tank wall under burst pressure. Noticeable is the formation of stress concentration zones in the vicinity of the neck, which makes this region more susceptible for initiating failure in the tank. This is also confirmed by examining the maximum principal stress, maximum shear stress, and Von-Mises equivalent stress as shown in Figure 4-4.

4.4 Multiple Tank Configurations

A second finite element analysis was performed on the six shape configurations shown in Figure 4.6. Such new design configurations provide more conformability since they can fit easily in any tight space. The new analysis consisted determining the required thickness for each design to reach a factor of safety of 2. The internal pressure applied to each wall tank is 15,000 psi and the material used was a carbon fiber/epoxy composite. The strength in the tensile direction of the composite material used was referenced as 180 ksi by the average of various unidirectional carbon fiber material properties.

Figure 4-6 Suggested design configurations.

(a) Sphere R=9.38"

(b) Cylinder with spherical ends

(c) 3-Cylinders with spherical ends

(d) 6 Spheres Compact

(e) 6 spheres Spaced

(f) 3 Interlocking Spheres

Figure 4-7 Stresses developed in various design configurations.

The stress field developed in each design configuration is illustrated by fringes as shown in Figure 4.7. High stress zones are formed within the vicinity of connections between different parts, which required a large wall thickness to accommodate such stress. This problem can be overcome by optimizing the size of the fillets between intersecting parts and tailoring the wall thickness to be thickened at these locations so that the stress concentration zones can be relieved and the required wall thicknesses of the new designs can be reduced. The thickness range needed for each design configuration is also shown on Figure 4-7.

Chapter 5

MANUFACTURING OF CARBON FIBER LINERS AND PRESSURE VESSEL SYSTEM FOR HYDROGEN STORAGE

5.1 Introduction

The objective of this phase of the project is to develop and manufacture a full-scale prototype of lightweight dense pressure vessels, both of spherical and cylindrical configurations, for hydrogen storage. The full-scale pressure vessels were to be tested by loading the tank to various pressure levels to measure the tank performance, while taking all necessary measures to ensure the safety of such experiments. In addition, possible collaboration with industrial partners was explored for gaining access to lab facilities suitable for testing such tank prototypes at internal service pressure levels of up to 15,000 psi and burst pressure of 33,800 psi to achieve the performance goals established by the USDOE for the year 2015.

Methods of producing pressure vessel systems by existing manufactures were extensively researched to understand common manufacturing methods. The most common manufacturing method for spherical or cylindrical geometries is filament winding. Therefore, it was necessary to have industrial quality prototyping of hydrogen storage tanks that rely on the design configurations developed earlier in Chapter Three to properly validate such theoretical predictions and demonstrate this technology. We could not secure the funds necessary to acquire a filament winding machine, which was absolutely necessary for this purpose. We negotiated with several manufacturers of composite pressure vessels the possibility of building the prototypes at their facilities; however the cost of such support from the industry exceeded the amount of funds that we had available for this project.

The goal of this phase of research turned to be devising a method to manufacture cylindrical and spherical pressure vessels in the laboratory facilities at West Virginia University.

5.2 Manufacturing Methods Search

A complex system such as a compressed gas storage system for hydrogen fuel initiatives is tailored by its strength and weight performance. Composite materials such as fiberglass and carbon fiber are beneficial over standard metal and alloy materials because of their exceptional strength and tailorability to design. Also, composite material applications are common for weight saving initiatives where excessive weight has unfavorable effects on the system in which the part is performing. A search was made to explore the most common techniques that can be used for prototyping process of the compressed gas tanks. This section presents a brief description of the various methods of manufacturing composites.

5.2.1 *Hand Lay-up*

The hand lay-up process is also referred to as a wet lay-up. It combines the reinforcement fibers with a liquid resin in a mold. Layers of fibers are placed into the mold and saturated with the resin. The part is hand rolled to create a uniform resin coat and extract any voids or air pockets within the combination. Layers are added until the thickness or desired orientation of fibers is reached. The curing process is the final stage of the hand lay-up manufacturing; it involves the chemical process of the resin changing state from a liquid to a solid (*Berbero, 1999*).

The lay-up process begins with the development of a proper mold to accommodate the desired part geometry and requirements of the curing process. The material used for a mold depends on the number of times the mold will be used, temperature and pressure of the curing process, and the manufacturing of the mold itself. To avoid the resin curing to the mold and damaging the finished part by forced removal, a release agent is applied to the areas where the mold and resin come into contact. Common release agents are wax, poly-vinyl alcohol, silicones, and release fabric.

The fibers are then placed on the mold to be saturated with resin. The proper measurements of mixing ratio of the resin and catalyst must be carefully followed and mixed thoroughly before application. After the different layers of fabric have been applied to the mold and saturated with the resin, hand rollers are used to compress the layers together and against the mold. Hand rolling of the lay-up ensures removal of any air pockets that will become voids during the curing process if not removed. The curing process is usually done at room temperature. However, elevated pressures are sometimes applied to the part during the curing process to remove excess resin and air via bag molding (*Berbero, 1999*).

5.2.2 *Bag Molding*

Pressure can be applied to a laminate during the curing process by using bag molding techniques. Vacuum bagging uses a flexible plastic or bag that is placed over the

laminate and sealed. A vacuum pump is connected so the air is pumped out from the inside of the bag which ultimately applies a uniform pressure onto the top surface of the laminate. The pressure forces the laminate against the mold creating an accurate resemblance to the mold geometry while removing excess resin and air. The three main methods of applying a pressure to a laminate are by pressure bag, vacuum bag, and autoclave manufacturing. Vacuum bagging is a popular manufacturing process because it is relatively inexpensive, allows large size parts to be manufactured, and the quality of the resulting part is mainly dependent on the manufacturer's skill and not a machining process (*Slobodzinsky, 1982*).

5.2.3 Autoclave Processing

Autoclave processing assists vacuum bag and pressure bag molding by applying heat and pressure to a laminate during the entire curing cycle. Curing pressures for autoclave processing are usually in the range of 50-100 psi (377.5-755 kg/m²). The benefits of autoclave processing are to produce a laminate with higher density and reduce the amount of time to completely cure a laminate. Autoclave processing is expensive, timely and laborious. The high cost of autoclave processing is a result of the autoclave itself, industrial gases such as nitrogen used for pressurization, and specialized lay-up materials that are not affected by elevated temperature and pressure. However, autoclave processing produces high quality, complex laminates and is beneficial for large parts and average production quantities. The method is very common in aerospace applications but for the research done at the university level, autoclaves are not as common because of the expense involved. An autoclave was not used for the research in this work because of cost reasons (*Meade, 1982*).

5.2.4 Compression Molding

Compression molding is a molding method in which the molding material, generally preheated, is placed in an open heated mold with matching male and female dies. The dies then close onto the material by the means of a hydraulic press, the assistance of heat and fairly high pressure cures the fibers and resin. After the part has completely cured the mold dies are lifted and the finished part is removed from the mold (*Young, 1982*). Compression molding is a fairly simple method which allows for high productive rates and moderate operation costs.

5.2.5 Pultrusion

Pultrusion is a continuous process for manufacturing composites with a continuous cross-sectional shape. In this process, fibers are impregnated with resin and carried through a die which forms the reinforcement to the desired shape and then heat is applied to cure the part (*Mallick, 1993*). Pultrusion is effective because it is inexpensive and can produce parts of any length by converting continuous fibers and resin into a solid laminate. The

process is performed by pulling continuous fibers through a heated die which shapes and cures the fiber and resin.

5.2.6 Resin Transfer Molding

Resin transfer molding (RTM) is an effective method to produce large continuous fiber composites. Complex shapes can be produced under short cycle times and the method provides the manufacturer with control of part specifications such as fiber orientation for optimum material properties (*Mallick, 1993*).

The RTM process is performed by a mold with ports to inject resin into the dry fiber and outlets which allow air to escape. The process consists of placing the dry fiber in the mold and closing it. The liquid resin is pumped into the closed mold until it is completely full. The ports are then sealed and heat is applied. After the part has cured, the mold is opened and the finished composite part can be removed (*Aström, 2002*).

5.2.7 Filament Winding

Filament winding is the oldest and most frequently considered process for machine dominated composite structures manufacturing (*Shen, 1995*). It is an automated process in which continuous filament is treated with resin and wound on a mandrel in a pattern which will provide strength in one direction (*Peters et al., 1991*). The process is performed by drawing the reinforcement from a spool or creel through a bath of resin, then winding it on the mandrel under controlled tension and in a predetermined pattern. The mandrel may be stationary, in which event the creel structure rotates above the mandrel, or it may be rotated on a lathe about one or more axes. By varying the relative amounts of resin and reinforcement, and the pattern of winding, the strength of filament wound structures may be controlled to resist stresses in specific directions. After sufficient layers have been wound, the structure is cured at temperature. The most common shapes to produce by this process are revolved surfaces such as pipes, cylinders, and spheres (*Lee and Suh, 2006*).

Filament winding uses continuous filaments or rovings in a revolving process around a mandrel to cover the surface of the mandrel geometry to a required thickness. Figure 5-1 shows the general concept of filament winding. As shown in Figure 5-1, the shape of the part produced takes the form of the mandrel. The need for a mandrel limits the shapes that can be produced, especially in cases where the mandrel needs to be removed after the winding process. Many types of mandrels have been developed to facilitate the removal process, while other designs utilize a metallic liner as a mandrel which is left as an integral part of the end product.

Figure 5-1 Filament winding process.

Due to the stipulation of an irremovable liner, the designs for the carbon fiber hydrogen storage system had to follow the requirement to utilize a liner which is left as an integral part of the final part. The work that follows describes the initiation cylindrical and spherical liners fabricated in the composites laboratory at WVU. The possibilities of initiating a filament winding facility at WVU were investigated by interacting with several winding facilities and manufacturers. Visits were made to two facilities:

- (1) Mclean Anderson Inc., a filament winding machine manufacturer.
- (2) Carleton Technologies Inc., pressure vessel manufacturer.

5.3 Quarter Cylindrical Tank Prototype

This prototype utilized hybrid-layered sandwich panel configurations to investigate suitable manufacturing techniques. A cylindrical tank section was created with a composite sandwich construction implementing access to the core structure via aluminum tube extrusions and thermal regulation by insulating foam as shown in Figure 5.2. The square cross section aluminum extrusions are equally segmented along the longitudinal axis of the cylinder and span the circumference of the tank. A composite sandwich structure was utilized for thermal regulation due to heat transitioning during hydrogen compression. The core structure also aids the tank design structurally by resisting displacements caused by internal pressure loading and increasing impact resistance.

Initiation of a core structure into the cylindrical tank design introduced ideas for temperature regulation and refueling. The aluminum extrusions are interconnected by the longitudinal tubing connecting to the circumferential tubing along the length of the tank. This system creates a port system to allow for continuous flow of a gaseous or liquid medium. This property of the design serves to aid in heat regulation by convective flow throughout the core section of the tank. Also, to address any issues of refueling at uneven

pressures within the tank, the ports could be directly connected to the interior of the tank cavity, creating several different input locations. The refueling process would pass through the core and into the tank cavity maintaining a steady pressure change within the volume.

(a) Outer Surface

(b) Inner Surface

Figure 5-2 Prototype of a quarter cylindrical tank section.

The ¼ section tank with a composite sandwich core design allows for various prototyping initiatives pertaining to heat regulation, increased stiffness due to core structure reinforcement, impact resistance and multiple ports refueling.

5.4 Field Visits

McLean Anderson

A visit to Mclean Anderson in Schofield, Wisconsin was taken to further understand the filament winding process and ultimately generate ideas for the hydrogen storage system project design and manufacturing methods. The points of interest during the visit were:

- Establishing a relationship with Mclean Anderson and initiating possibilities of a partnership for manufacturing.
- Understanding the details of filament winding such as materials used, automation control of winding process, costs, manufacturing time, part curing procedures, etc.
- View filament wound parts made by Mclean Anderson and understanding their advantages and limitations.
- Pricing of specific Mclean Anderson filament winding machines to be used at the composites laboratory at WVU.

Carleton Technologies Inc

Carleton Pressure Technology Division (Carleton PTD) is located in Westminster, Maryland and manufactures a full line of lightweight composite pressure vessels that are used in space, marine, aircraft, and life support and paintball applications. A visit was taken to this facility in order to discuss the possibilities for manufacturing lightweight composite high pressure vessels for hydrogen storage.

5.5 Liner Manufacturing

The development of a liner for the hydrogen storage system proved to be a challenging task due to material reactions with hydrogen, manufacturing capabilities of a seamless or weld-free liner, and cost requirements. The desired pressure level of 30,000 psi will require the development of liners that combine the properties of chemical compatibility and low hydrogen permeation. Identifying a suitable material candidate for the liner involved researching existing developments in the hydrogen storage field and the analysis of possible liner materials and their reaction with hydrogen at high pressures and various temperature levels. Some of these requirements have previously been met in lightweight pressure vessels utilized in various space and missile systems with liners made from relatively high yield strength materials such as titanium, Inconel, and Stainless steel.

Such high yield strength materials have been used to allow the liners to cycle elastically during operation (Veys *et al.*, 1989). Aluminum was also considered a desirable liner material due to its moderate cost and low density. Aluminum's modulus of elasticity and relatively low yield strength precluded its use as a liner material in space system (Veys *et al.*, 1989). However, our field visits to manufacturers' facilities as well as previous research indicated that aluminum was utilized successfully in constructing pressure vessels with an operating pressure of up to 10,000 psi. High-density polyethylene, thermoplastics (Struble, 2007), ultra-high molecular polymer (Sirosh, 2002) were also reported as candidate for a liner materials for high pressure storage vessels.

Research involving the selection of a liner material and manufacturing the liner geometry to later implement filament winding were performed in parallel. As previously mentioned, the liner will serve as the mandrel geometry during a filament winding composite manufacturing process. Thus, the work at hand has included the development of a cylindrical and spherical liner.

The initial stages of fabricating a prototype of a hydrogen storage vessel focused on devising methods to create a ¼ section of a carbon fiber storage vessel. The main goal at this stage was to build hand-on experience with the manufacturing process and to experimentally verify the performance characteristics of the preliminary designs developed in this project.

5.5.1 Cylindrical Liner

To manufacture a cylindrical liner through a wet composite layup process involved using a cylindrical mold which also allowed removal of the liner from the mold. A steel cylindrical pressure vessel was used as the mold for the composite layup. The manufacturing process was done in phases because creating the liner in a single part construction would not allow removal from the mold, therefore two end caps and a cylindrical body were created with post-cure assembly as depicted in Figure 5-3 (a). The inner dimensions of the cylindrical liner are shown in Figure 5-3 (b). The assembly of the liner was reinforced by secondary bonding in the regions show in Figure 5-3 (a).

Figure 5-3 Manufacturing of a composite cylindrical liner.

5.5.2 Spherical Liner

A similar process was followed to lay up a composite spherical liner. The spherical liner used a bowling bowl as a mold to create two half spheres to be assembled by fit and secondary bonding as illustrated in Figure 5-4 (a). The inner dimensions of the spherical liner are shown in Figure 5-4 (b).

Figure 5-4 Manufacturing of a composite spherical liner.

The assembly of each liner demanded a tolerance fit between the end domes and the cylindrical body for the cylindrical liner and for the half spheres of the spherical liner. The spacing for each was created by introducing a spacer on the mold for the end domes to cover the thickness of the cylindrical body and repeating for the second end of the spherical liner.

Figure 5-5 Carbon fiber cylindrical and spherical liner systems.

The cylindrical and spherical liners were manufactured with 2×2 twill weave 3k carbon fiber dry fabric and epoxy resin matrix. Two layers of carbon fiber were applied to each section of the cylindrical and spherical liners. Figure 5-5 displays the cylindrical and spherical carbon fiber parts to be used as the liner geometry of a composite pressure vessel.

5.6 Spherical Pressure Vessel

As the industrial production of filament wound spherical and cylindrical prototypes turned to be not possible due to budgetary constraints, methods to create a spherical composite pressure vessel were analyzed based on manufacturing techniques, lab facilities and equipment, and cost. The initial construction of the cylindrical and spherical liners followed compatibility with filament winding techniques and manufacturing processes. To utilize the facilities available at WVU and initiate a continuous, spherical composite pressure vessel alternative manufacturing methods to filament winding had to be initiated. A unique approach which invokes continuous braided carbon fiber sleeves layered over the spherical liner was implemented as an effective manufacturing technique to resist the loads induced by high internal pressure loading. Braided carbon fiber is effective for manufacturing various composite geometries because the biaxial braid can repeatedly expand to fit over molds or cores. The material specifications of the carbon fiber sleeve material used for prototyping can be summarized as follows:

Material: Carbon Fiber Biaxial Braided Sleeve

Fiber Orientation: $\pm 45^\circ$

Size: 8 inch diameter

Weight: 14.3 oz/sq. yd

A braided composite sleeve can accommodate straight, uniform cross section forms as well as non-linear irregular cross section structures. Figures 5.6 to 5.8 show the manufacturing method used to produce the spherical tank prototype.

The first step in the manufacturing process was to refine the spherical liner to be free of burrs or unsmooth regions that would inhibit the sliding of the carbon fiber sleeve over the liner. A wet-layup composite manufacturing process often produces free fibers along the edges of the cut carbon fiber fabric and when cured in resin the free fibers create a rough surface. Figure 5.6 shows the sanding and preparation of the spherical liner to create a smooth exterior surface conducive to sliding the resin impregnated sleeve over the liner.

Figure 5-6 Carbon fiber cylindrical and spherical liner systems.

The ports for the piping into the spherical vessel were next applied to the liner halves as shown in Figure 5-7. Hysol adhesive was placed around the necking of the port to connect the port to the liner and simultaneous creating a filleted region to allow a smooth transition of the carbon fiber sleeve over the tank geometry, as depicted in Figure 5-7 (a). The two liner halves were then joined by adhesive bonding with the finished liner and piping shown in Figure 5-7 (b).

(a) Assembly of Piping to Spherical Liner

(b) Liner and Pipe

Figure 5-7 Assembly of piping to spherical liner.

The layup process for the spherical vessel is shown in Figure 5.8. First, all layup materials were organized and placed to quickly assemble the resin impregnated carbon

fiber sleeve, Figure 5.8 (a). The resin used has a 60 minute cure time therefore; the layup process from start to finish should be within this time period for an effective and structurally sound composite part. Once all initial preparations were complete, the carbon fiber sleeve was wetted with epoxy resin and applied over the liner as seen in Figure 5.8 (a) to (d). This process was repeated for ten layers, to avoid slipping of underneath layers during the application of the most top layer. Each end was clamped to the piping which kept the layer and tension and orientated properly.

(a) Mounting of spherical liner

(b) Wetting of sleeve with resin

(c) Application of sleeve over liner

(d) Adding another sleeve

Figure 5-8 Laying up spherical storage tank.

The finished spherical vessel is shown below in Figure 5-9. Figure 5-9(a) displays a side-view of the spherical geometry with both tapered port sections. The port/valve connection is shown in Figure 5-9(b) along with the sectioned thickness of the carbon fiber sleeve. The thickness dimension of the spherical vessel was determined from theoretical finite element modeling and experimental analysis performed of carbon fiber sample sections. The analysis confirmed that the thickness of 0.8 inch and inner diameter of 8.5 inches would resist high intensity internal pressure loading of 30,000 psi.

(a) Side view

(b) Port/Valve Connection

Figure 5-9 All carbon-fiber spherical pressure vessel.

5.7 Mechanical Testing

Sheets of carbon fiber were laid up using the same technique and carbon fiber material used in building the spherical pressure vessel in order to get coupon specimens that can be used in material characterization. Figure 5.10 illustrates the final composite plates as well as the coupon specimens after they were cut from such plates.

Figure 5-10 Carbon-fiber specimens used for material testing.

Plates were made of thicknesses of 0.375 inch (10 mm) and 0.875 inches (18 mm). Coupon specimens were cut to have one inch in width and 10 inches in length. Each specimen was fitted in its middle with two wire resistance strain gages on top and bottom as shown in Figure 5.10. Standard uniaxial tensile tests as well as 4-point bending tests were performed on such specimens as shown in Figure 5.11 in order to determine the tensile strength of each specimen.

(a) Four-Point Bending Test Setup

(b) Uniaxial Tensile Test Setup

Figure 5-11 Uniaxial tensile and four-point bending testing setups.

5.7.1 Four-Point Bending Tests

In Four-point loading test, the specimens were loaded as shown in Figure 5.12 and strains were measured at top and bottom as the load increases. The stresses were calculated and the stress-strain diagrams were generated. The middle region of the beam is under a uniform bending moment, which produces a failure mode in this region that is independent on the effect of shearing force due to the reaction at the supports.

(a) Deformed specimen

(b) Bending moment diagram

Figure 5-12 Deformed specimens in four-point bending test.

Under the effect of the applied load, P , the maximum bending moment is calculated by:

$$M = Pa / 2 \quad (5.1)$$

and the flexural stress at top or bottom can be calculated as:

$$\sigma = (M / I) h / 2 \quad (5.2)$$

The strain due to bending, ε_b , can be calculated from the measured strains by:

$$\varepsilon_b = \frac{\varepsilon_{top} - \varepsilon_{bottom}}{2} \quad (5.3)$$

The testing results of specimens with thicknesses 0.375 inch (10 mm) and 0.875 inch (18 mm) are presented in Figures 5-13 and 5-14 respectively. It can be noticed that 0.375 inch thick specimens were failed in compression in top fibers as in Figure 5-13 (c), while the 0.875 inch thick specimens failed by interlaminar shear as shown in Figure 5-14 (c). None of the specimens was failed in tension. This indicates that the calculated strength from such test represent the lower bound value for the tensile strength of such a carbon fiber composite that was used for the tank prototype. The stress-strain diagrams for both

specimens, shown in Figures 5-13 (b) and Figure 5-14 (b), indicate linear relationships up to failure.

(c) Failure Mode

Figure 5-13 Four-point bending test of 10 mm thick specimens.

Based on the results shown in Figure 5-13 and Figure 5-14, it is clear that using the manufacturing technique for laying up carbon fiber laminates followed here, a laminate tensile strength of 84.5 ksi is achievable. As mentioned earlier, this value may underestimate the actual tensile strength since none of the specimens failed in tension. Adopting such strength value in pressure vessel design, one could estimate the corresponding burst pressure in spherical tank using Equation (5.4) as follows:

$$\sigma_{max} = \frac{P \times r_{tank}}{t_{tank}} \quad (5.4)$$

where P is the expected magnitude of the burst pressure, r_{tank} is the vessel radius, and t_{tank} is the vessel wall thickness.

(a) Tensile and Compressive Strains

(b) Stress-Strain Diagram

(c) Failure Mode

Figure 5-14 Four-point bending test of 18 mm thick specimens.

5.7.2 Uniaxial Tension Tests

Specimens of dimensions similar to those used in four-point bending tests were subjected to uniaxial tensile test as depicted in Figure 5.11 (b). However, holding such specimens by the grips of the testing machines was so difficult. As a result, these specimens failed at the grips. The top layer of the carbon fiber laminate was broken at this location

6.1 Introduction

A comprehensive review of theoretical models described in the literature for predicting the effects of various damage mechanisms on the residual properties of isotropic or composite materials has been completed. Its primary objective is to ensure that the best suitable approach is implemented in this project for predicting the fatigue life and damage tolerance of hydrogen storage tanks, by leveraging existing knowledge effectively, and focusing the effort on developments related directly to the specific loading and geometric characteristics of such systems. The main findings of the review conducted so far are summarized below.

An early definition of damage was proposed by Kachanov (1958), which may be interpreted as effective surface density of micro-damages per unit volume. He pioneered the concept of continuum damage mechanics by introducing the concept of effective stress. This concept is based on considering a fictitious undamaged configuration of an element and comparing it with the actual damage configuration.

Several other approaches were presented since then, by taking in consideration couplings between several parameters and effects. The simplest of these approaches considers only isotropic materials and small deformations. Alfredsson and Stigh (2004), Basaran and Nie (2204), Basaran and Tang (2002), considered small deformations in an isotropic material, coupled with thermal properties for predicting the effects of low cycle fatigue loads.

Anisotropic damage models coupled with plasticity and small deformations were developed by Abu Al-Rub and Voyiadis (2003), Castagne, *et al.* (2003), Chow and Yang (2004), Contraffatto and Kuomo (2002), Isaakson, *et al.* (2004), and Lestriez, *et al.* (2004). All these models were implemented in finite element software. Hammi *et al.* (2004) have developed an anisotropic damage model for rate-dependent plasticity. Brünig (2002 and 2003) analyzed a nonlinear continuum damage mechanics model, where large strain elastic-plastic deformation behavior of ductile metals damaged in an anisotropic pattern was considered.

Chan, *et al.* (1977), modeled anisotropic damage for creep failure and cleavage. Chen (2004) studied the evolution of localized failure in tertiary creep in a coupled

viscoplasticity–damage model. Also, Kawai (2002) developed a phenomenological constitutive model to describe creep and damage behavior characteristics that deviate from the von Mises type of stresses for a class of polycrystalline materials.

The use of a gradient theory in such model can avoid the localization of damage, which leads to a mesh-dependence of the finite element analysis, Santaoja (2000b), Voyiadis *et al* (2003b). Gradient theories with proper length scales can formulate a constitutive framework at the continuum level that is used to bridge the gap between different physical scale levels. However, it is still not possible to perform quantum or atomistic simulations on realistic time and structures, Voyiadis *et al* (2003a).

The review of all the various approaches presented in the literature for a wide variety of special cases leads to the conclusion that, for the purpose of this research effort, it is desirable to integrate several suitable approaches into a single model. Such coupling between the effects of different damage mechanisms will allow us to develop a comprehensive continuum damage mechanics approach and related software that is associated with plasticity, viscoelasticity, low cycle fatigue, finite deformation and thermal effects that are to be expected during the operation of hydrogen storage tanks made of metals, composites, or hybrid metal/composite materials.

The basic approach selected for developing such an integrated model is based on thermomechanics principles. The complexity of the model is directly determined by the form of the Helmholtz free energy, the number of conjugate pairs of variables, and the type of failure to be predicted. In all cases, a verification of the material model, expressed by the Helmholtz free energy, may include the following steps:

- (1) Select the set of mutually independent state variables for a certain particular material model. For the case of small deformations, this could be $\{\varepsilon, \varepsilon^i, \theta, a^{(k)}\}$, which refers to the total strain, inelastic strain, temperature and other $k=1..,n$ internal variables.
- (2) Write the explicit forms for the two potentials for the selected material model.
 - (a) Specific Helmholtz free energy or
Specific Gibbs free energy
 - (b) Specific dissipation function,
Specific complementary dissipation function, or
Yield function F .

In the case of this project, it was decided to use the specific Helmholtz free energy and the Yield functions as the constraint function.

- (3) Apply State Equations.
- (4) Apply Normality Rule.
- (5) Verify the satisfaction of the Clausius- Duhem inequality (or the thermodynamic laws).

After the model is verified, it is ready to be implemented in a finite element code.

A rigorous mathematical analysis has been carried out in the past few months in order to define clearly all the steps shown above. In addition, several simple models have been already developed for the following conditions:

- Isotropic-thermo-elasticity.
- Von Mises plasticity.
- Hooke's law, thermal expansion, and creep.

The extension from these special-purpose models to a fully coupled damage model is straightforward. An extension of the isotropic material model to a composite configuration could be done by several methods. The one that will be implemented in the present work models the material by using the Serial/Parallel mixing theory, which obtains the composite behavior from the constitutive laws of its components. This will allow us to use directly the coupled material model when composites are modeled and analyzed in a finite element code.

6.2 Themomechanics

The concepts and principles of thermodynamics when combined with those in continuum mechanics lead us to the concept of thermomechanics. The first step is the definition of a set of mutually independent state variables. After considering additive decomposition of the strains due to small deformations, as seen in Figure 6-1, the total strain is considered in a general case as

Figure 6-1 Additive strain decomposition for small deformations.

$$\varepsilon_{ij} = \varepsilon_{ij}^p + \varepsilon_{ij}^e \quad (6.1)$$

A set of specific thermodynamic potentials are related through the Legendre transformation. Also, this transformation relates the internal state variables with its correspondent thermodynamic forces. Table 6-1 shows the internal energy, Helmholtz free energy and Gibbs free energy relations with their state equations.

Table 6-1 Specific thermodynamic potentials for small deformations in continuum mechanics.

	Internal energy	Helmholtz free energy	Gibbs free energy
	$u = u(\varepsilon_{ij}, \varepsilon_{ij}^p, s, a^{(k)})$	$\psi = \psi(\varepsilon_{ij}, \varepsilon_{ij}^p, \theta, a^{(k)})$ $= u - s\theta$	$\zeta = \zeta(\sigma_{ij}, \theta, a^{(k)})$ $= \psi - \sigma_{ij}\varepsilon_{ij}^e$
<i>State Equations</i>	$\sigma_{ij} = \rho \frac{\partial u}{\partial \varepsilon_{ij}^e}$	$\sigma_{ij} = \rho \frac{\partial \psi}{\partial \varepsilon_{ij}^e}$	$\varepsilon_{ij}^e = -\rho \frac{\partial \zeta}{\partial \sigma_{ij}}$
	$\theta = \frac{\partial u}{\partial s}$	$s = -\frac{\partial \psi}{\partial \theta}$	$s = -\frac{\partial \zeta}{\partial \theta}$
	$A^{(k)} = -\rho \frac{\partial u}{\partial a^{(k)}}$	$A^{(k)} = -\rho \frac{\partial \psi}{\partial a^{(k)}}$	$A^{(k)} = -\rho \frac{\partial \zeta}{\partial a^{(k)}}$

A model is best defined using the specific Helmholtz free energy as the thermodynamic potential than the internal energy potential because it is difficult to measure the entropy. Generally the Helmholtz free energy is used as the potential, so for the case of small deformations the set of internal state variables for a general case are defined as

$$(\varepsilon_{ij}, \varepsilon_{ij}^p, \theta, a^{(k)}) \quad (6.2)$$

which refers to the total strain, inelastic strain, temperature and $k=1,2,\dots,n$ other internal variables. The parameter $a^{(k)}$ could be a scalar, vector, tensor, or function as defined accordingly to the problem to be analyzed.

After applying conservation of mass, balance of linear momentum, balance of moment of momentum, first law of thermodynamics, and second law of thermodynamics considering small deformations and using the Helmholtz free energy and the internal state variables defined in Eq. (6.2), the Clausius-Duhem inequality is obtained as

$$\sigma_{ij} \dot{\varepsilon}_{ij}^p + \sum_{k=1}^n A^{(k)} \dot{a}^{(k)} - q_i \frac{\theta_{,i}}{\theta} \geq 0 \quad (6.3)$$

Since the entropy generation in time is always increasing then each of the components of Eq. (6.3) must also be nonnegative. So, always

$$\left\{ \begin{array}{l} \sigma_{ij} \dot{\varepsilon}_{ij}^p \geq 0 \\ A^{(k)} \dot{a}^{(k)} \geq 0 \\ -q_i \frac{\theta_{,i}}{\theta} \geq 0 \end{array} \right. \quad (6.4)$$

must be satisfied. If the model is simple, an analytical prove of Eq. (6.4) could be done. If this proof is not trivial, a numerical validation of Eq. (6.4) must be done. In this case, the validation will be done numerically.

A yield potential function f is used in order to minimize the potential and the growth of the dissipation as expressed in Eq. (6.4). This yield potential is defined considering only local and not heat conduction phenomena. In order to minimize this local dissipation phenomenon, the Lagrange multipliers and Legendre transformation concepts are used. After applying the normality rule (Lagrange) and verifying the homogeneity (Legendre) and convexity of f , the evolution of the internal state variables and Legendre multiplier must satisfy

$$\left\{ \begin{array}{l} \dot{\varepsilon}_{ij}^p = \sum_{i=1}^m \dot{\lambda}^{(i)} \frac{\partial f^{(i)}(\sigma_{ij}, A^{(k)})}{\partial \sigma_{ij}} \\ \dot{a}^{(k)} = \sum_{i=1}^m \dot{\lambda}^{(i)} \frac{\partial f^{(i)}(\sigma_{ij}, A^{(k)})}{\partial A^{(k)}} \\ \dot{\lambda}^{(i)} \geq 0 \end{array} \right. \quad (6.5)$$

where for a general case more than one yield potential can be used $i=1, 2, \dots, m$.

6.3 Damage

The basic definition of damage, exposed by early work of Kachanov (1958) and (1986), and newer ones done by Krajcinovic (1996), Lemaître and Desmorat (2005), or Voyiadjis and Kattan (2005), expresses damage as a macroscopic measure. Damage is basically characterized by three mechanisms of microdamages growth: (i) nucleation of microscopic voids that initiate at inclusions and second phase particles, failure of particles or microcracking of the matrix surrounding the inclusion, (ii) growth of the microvoids by means of plastic strain and hydrostatic stress, and (iii) coalescence or microcracks linking the growing microvoids with adjacent ones, thus leading to vanishing

load carrying capacity of the material, as the damage density approaches unity or a critical failure value.

When a uniaxial isotropic damage is considered, only one damage parameter that relates the damaged and undamaged configurations D is used. This is defined as the ratio between the most critical area where all cracks and voids are removed over the whole RVE (representative volume element), A^D , and the initial (or damaged) area, so

$$D = \frac{A^D}{A} = \frac{A - \bar{A}}{A} = 1 - \frac{\bar{A}}{A} \quad (6.6)$$

If all types of damage, including voids and cracks, are removed from the RVE, one fictitious undamaged (effective) configuration is obtained, Figure 6-2(b). Since both configurations are subjected to the same external load T , then

$$\sigma A = \bar{\sigma} \bar{A} \quad (6.7)$$

then,

$$\bar{\sigma} = \frac{1}{(1-D)} \sigma \quad (6.8)$$

Figure 6-2 Remove of Cracks and Voids from the Representative RVE.

Also, must be noted that the stress-strain relations for the damaged and undamaged configurations are

$$\begin{cases} \sigma = E \varepsilon \\ \bar{\sigma} = \bar{E} \bar{\varepsilon} \end{cases} \quad (6.9)$$

Usually an energy approach is used in the literature in order to define completely the equivalence between both configurations. This approach stated that the elastic strain energy is the same in both configurations, Cordebois and Sidoroff (1979).

Under a threshold value defined in point A in Figure 6-3 no damage is developed, then no difference between both configurations is observed. When the load is increased over the threshold value, damage will be produced and increased, i.e. in Figure 6-4(b) a damaged area is developed inside de RVE. If the load is continuously increasing until point C, damage is developing and the damaged area could be referred to the previous point as

$$A_C^D = A_B^D + \Delta A_{BC}^D \quad (6.10)$$

Figure 6-3 Elastic strain-energy density equivalence between damaged and effective configurations.

If the loading reaches point C and then is reduced to zero, O, no damage is developed. When point O is reached all cracks are closed but not healed, Figure 6-4(e). Within OC a linear elastic behavior is observed, but with a different stiffness from OA due to the increment of damage, so

$$A_C^D = A_P^D = A_{OC}^D \quad (6.11)$$

Figure 6-4 Damage evolution according to Figure 6-3.

If the loading is increased above the actual threshold value, C , damage is developed until an ultimate point is reached, U . In this point a critical damage value is obtained, where values beyond this cannot be obtained because failure has been reached.

Since the elastic strain energy is considered the same for both configurations, and taking into account that in both configurations a linear behavior is observed, then according to Figure 6-3 the areas OAM , APQ , and $O'M'N'$ have the same value. Moreover, since the relation between the effective stress and undamaged stress was defined in Eq. (6.8), and using the relations for damaged and undamaged configurations in Eq. (6.9), a relation between the stiffness in both configurations is obtained as

$$E = (1 - D)^2 \bar{E} \quad (6.12)$$

Three mechanisms of failure are seen in composite materials, fiber breakage, inter-fiber failure and delamination. The external loadings that induce to these failures are seen in Figure 6-5, which were defined by Papanikos, *et al* (2003).

The three failure mechanisms are considered independent from each other. This means that the damage components in the three orthogonal directions, 1, 2, and 3, evolves without taking into account the damage evolution of the others. So, fiber breakage would not induce delamination neither inter-fiber failure.

When FRP (fiber reinforced plastics) is considered the damage principal direction, 1, is coincident with the fiber direction. This allows considering always fiber failure, interfiber failure and delamination be coincident with the principal directions 1, 2, and 3 correspondly. Also due to this damage visualization, the damage second-order tensor will be a diagonal tensor, defined as

$$D_{ij} = d_i \delta_{ij} \quad (\text{no sum on } i) \quad (6.13)$$

Figure 6-5 Composite materials failure mechanisms.

Barbero (2008) defines an integrity second-order tensor and then the fourth-order damage effective tensor and its inverse as

$$\Omega_{ij} = \sqrt{I_{ij} - D_{ij}} = \sqrt{\delta_{ij} - d_i \delta_{ij}} = \sqrt{1 - d_i} \delta_{ij} = \Omega_i \delta_{ij} \quad (6.14)$$

$$M_{ijkl} = \frac{1}{2} (\Omega_{ik} \Omega_{jl} + \Omega_{il} \Omega_{jk}) = \sqrt{1 - d_i} \sqrt{1 - d_j} I_{ijkl} = \Omega_i \Omega_j I_{ijkl} \quad (6.15)$$

$$M_{ijkl}^{-1} = \frac{1}{\sqrt{1 - d_i} \sqrt{1 - d_j}} I_{ijkl} = \frac{1}{\Omega_i \Omega_j} I_{ijkl} \quad (6.16)$$

where no sum on i, j is considered.

The relations between the damaged and effective configurations are then stated as,

$$\begin{cases} \sigma_{ij} = M_{ijkl} \bar{\sigma}_{kl} \\ \varepsilon_{ij}^e = M_{ijkl}^{-1} \bar{\varepsilon}_{ij}^e \\ C_{ijkl} = M_{ijn} \bar{C}_{mnpq} M_{pkql} \end{cases} \quad (6.17)$$

where $\mathbf{C}$ and $\bar{\mathbf{C}}$ are the fourth-order damaged and effective stiffness tensors, respectively.

6.4 Plasticity

The yield surface specifies the state of stress at which plastic flow initiates. This surface is generally defined as a function g , so $g=0$ indicates plastic evolution. Negative values are given when an elastic behavior occurs, and nonnegative values are not admissible for rate-independent plasticity.

Figure 6-6 Yield surface definition.

For a simple uniaxial case, as seen in Figure 6-6, the strain stress curve is used to define a plastic strain stress curve. Observe that after an initial threshold value S_y plastic evolution will occur, and this value and under only elastic behavior is seen. This new curve is used to define the yield surface, as

$$g(\sigma, R) = \hat{g}(\sigma) - \hat{R}(R) \quad (6.18)$$

where $\hat{g}$ represents the state the positive value of the stress $\hat{g} = \sqrt{\sigma}$ for the case of uniaxial stress or an equivalent positive value of the state of stresses. $\hat{R}$ represents the limit where plasticity occurs and this evolution is presented in Figure 6-6, so

$$\hat{R} = R + R_0 \quad (6.19)$$

A flow rule was specified in Eq. (6.5), which relates the internal state variable rate as a function of the partial derivative of a yield potential f with respect to its thermodynamic force. This rate and partial derivative are linearly related to a Lagrange multiplier. This multipliers and the yield surface g are restricted by the Kuhn-Tucker conditions, which are classic in the convex mathematical programming literature, and states that

$$\begin{cases} \dot{\lambda} \geq 0 \\ g \leq 0 \\ \dot{\lambda} g = 0 \end{cases} \quad (6.20)$$

Figure 6-7 Kuhn-Tucker and consistency conditions

After differentiating $\dot{\lambda} g = 0$ and for case of pure plastic evolution, $g=0$, a final condition is obtained. This is usually called consistency or persistency condition and defined as,

$$\dot{\lambda} \dot{g} = 0 \quad (6.21)$$

All this conditions are represented in Eq. (6.7), where elastics behavior and plastic evolution are clearly observed. When elastic behavior is expected, the value of the plastic surface should be a negative value and the multiplier should be zero, or no plastic flow will occur. If the multiplier is zero but the yield surface value is positive represents a non possible state. So, the multiplier must increase and the yield value must go to zero in order to reach a plastic evolution state. At this point, the rate of change of the yield surface must be zero.

6.5 Damage-Plasticity

Until this point, general concepts have been defined and exposed. All this concepts will now be integrated in a method in order to produce a material model. In general the following steps are to be followed to define completely the model.

The definition of the state variables and the form of the specific Helmholtz (or Gibbs) free energy potential constitutes a break point on the formulation, since they are the basis for the derivation of all the constitutive equations.

- Step 1:* Select the state variables.
- Step 2:* Define the specific Helmholtz (or Gibbs) free energy potential.
- Step 3:* Apply the state equations to evaluate the thermodynamic forces and its rates.
- Step 4:* Apply the normality rule to evaluate the state variables rates.
- Step 5:* Define the yield surfaces.
- Step 6:* Find the Jacobian after applying the Kuhn-Tucker and consistency conditions.
- Step 7:* Implement the iterative variables used to obtain the Lagrange multipliers numerically. We will use the Newton-Raphson method and not the return mapping algorithm.

Since we are interested in a uniaxial fiber composite material model all the steps defined will be developed in the basis of this model in mind. Also, a 3-D model will be considered.

Step 1

A plastic strain and damage state variables are considered. Damage will be taken as that defined in Eqs. (6.13) through (6.17). An isotropic hardening plasticity p and a correspondent isotropic hardening damage δ are considered, then the state variables are expressed as,

$$\psi(\varepsilon_{ij}, \varepsilon_{ij}^p, D_{ij}, p, \delta) \quad (6.22)$$

Step 2

The Helmholtz free energy is defined as 3 different potentials. An elastic one deduced from the strain energy density, a plastic-strain energy dissipation density, and a damage

energy dissipation density. All three are considered independent to each other so the evolution of each state variable is clearly defined, so

$$\psi = \psi_e(\varepsilon_{ij}, \varepsilon_{ij}^p, D_{ij}) + \psi_p(p) + \psi_d(\delta) \quad (6.23)$$

where,

$$\begin{cases} \psi_e = \psi_e(\varepsilon_{ij}, \varepsilon_{ij}^p, D_{ij}) = \frac{1}{2\rho} (\varepsilon_{ij} - \varepsilon_{ij}^p) C_{ijkl} (\varepsilon_{kl} - \varepsilon_{kl}^p) = \frac{1}{2\rho} \varepsilon_{ij}^e C_{ijkl} \varepsilon_{kl}^e \\ \psi_p = \psi_p(p) = \frac{1}{\rho} \sum_{i=1}^{n_p} \alpha_i^p \left(-\beta_i^p e^{\left(\frac{p}{\beta_i^p}\right)} + p \right) \\ \psi_d = \psi_d(\delta) = \frac{1}{\rho} \sum_{i=1}^{n_d} \alpha_i^d \left(-\beta_i^d e^{\left(\frac{\delta}{\beta_i^d}\right)} + \delta \right) \end{cases} \quad (6.24)$$

where α_i^p , β_i^p , α_i^d , and β_i^d are material parameters, when the plastic and damage potentials are defined as n -terms Prony series.

Step 3

Applying the state equations, the following set of equations are obtained,

$$\begin{aligned} \sigma_{ij} &= \rho \frac{\partial \psi}{\partial \varepsilon_{ij}^e} = \rho \frac{\partial \psi_e}{\partial \varepsilon_{ij}^e} = \rho \frac{\partial}{\partial \varepsilon_{ij}^e} \left(\frac{1}{2\rho} \varepsilon_{kl}^e C_{klmn} \varepsilon_{mn}^e \right) = C_{ijkl} \varepsilon_{kl}^e = C_{ijkl} (\varepsilon_{kl} - \varepsilon_{kl}^p) \\ Y_{ij} &= -\rho \frac{\partial \psi}{\partial D_{ij}} = -\rho \frac{\partial \psi_e}{\partial D_{ij}} = -\rho \frac{\partial}{\partial D_{ij}} \left(\frac{1}{2\rho} \varepsilon_{kl}^e C_{klmn} \varepsilon_{mn}^e \right) = -\frac{1}{2} \varepsilon_{kl}^e \frac{\partial C_{klmn}}{\partial D_{ij}} \varepsilon_{mn}^e \\ &= -\frac{1}{2} (\varepsilon_{kl} - \varepsilon_{kl}^p) \frac{\partial C_{klmn}}{\partial D_{ij}} (\varepsilon_{mn} - \varepsilon_{mn}^p) \\ R &= -\rho \frac{\partial \psi}{\partial p} = -\rho \frac{\partial \psi_p}{\partial p} = -\rho \frac{\partial}{\partial p} \left[\frac{1}{\rho} \sum_{i=1}^{n_p} \alpha_i^p \left(-\beta_i^p e^{\left(\frac{p}{\beta_i^p}\right)} + p \right) \right] = \sum_{i=1}^{n_p} \alpha_i^p \left(e^{\left(\frac{p}{\beta_i^p}\right)} - 1 \right) \\ \gamma &= -\rho \frac{\partial \psi}{\partial \delta} = -\rho \frac{\partial \psi_d}{\partial \delta} = -\rho \frac{\partial}{\partial \delta} \left[\frac{1}{\rho} \sum_{i=1}^{n_d} \alpha_i^d \left(-\beta_i^d e^{\left(\frac{\delta}{\beta_i^d}\right)} + \delta \right) \right] = \sum_{i=1}^{n_d} \alpha_i^d \left(e^{\left(\frac{\delta}{\beta_i^d}\right)} - 1 \right) \end{aligned} \quad (6.25)$$

The rate of the thermodynamic forces defined when the rule chain is used with respect to its respectively variables are defined as,

$$\begin{aligned}
\dot{\sigma}_{ij} &= \frac{d\sigma_{ij}(\varepsilon_{ij}, \varepsilon_{ij}^p, D_{ij})}{dt} = \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}} \dot{\varepsilon}_{kl} + \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}^p} \dot{\varepsilon}_{kl}^p + \frac{\partial \sigma_{ij}}{\partial D_{kl}} \dot{D}_{kl} \\
\dot{Y}_{ij} &= \frac{dY_{ij}(\varepsilon_{ij}, \varepsilon_{ij}^p, D_{ij})}{dt} = \frac{\partial Y_{ij}}{\partial \varepsilon_{kl}} \dot{\varepsilon}_{kl} + \frac{\partial Y_{ij}}{\partial \varepsilon_{kl}^p} \dot{\varepsilon}_{kl}^p + \frac{\partial Y_{ij}}{\partial D_{kl}} \dot{D}_{kl} \\
\dot{R} &= \frac{dR(p)}{dt} = \frac{\partial R}{\partial p} \dot{p} \\
\dot{\gamma} &= \frac{d\gamma(\delta)}{dt} = \frac{\partial \gamma}{\partial \delta} \dot{\delta}
\end{aligned} \tag{6.26}$$

Also,

$$\dot{\sigma}_{ij} = \frac{d}{dt} [C_{ijkl} (\varepsilon_{kl} - \varepsilon_{kl}^p)] = C_{ijkl} \dot{\varepsilon}_{kl} - C_{ijkl} \dot{\varepsilon}_{kl}^p + \dot{C}_{ijkl} \varepsilon_{kl}^e \tag{6.27}$$

then, equating Eqs (6.27) and (6.26a), the following relations are obtained,

$$\left\{ \begin{array}{l} \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}} = C_{ijkl} \\ \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}^p} = -C_{ijkl} \\ \frac{\partial \sigma_{ij}}{\partial D_{kl}} \dot{D}_{kl} = \dot{C}_{ijkl} \varepsilon_{kl}^e \end{array} \right. \tag{6.28}$$

and finally the stress rate is reduced to,

$$\dot{\sigma}_{ij} = C_{ijkl} \dot{\varepsilon}_{kl} - C_{ijkl} \dot{\varepsilon}_{kl}^p + \frac{\partial \sigma_{ij}}{\partial D_{kl}} \dot{D}_{kl} \tag{6.29}$$

Step 4

Two yield potentials are defined, one related to the plastic evolution and other to the damage evolution. As in the case of the Helmholtz free energy potential both potentials develop independently from each other, then

$$\left\{ \begin{array}{l} f_p(\sigma_{ij}, R) \\ f_d(Y_{ij}, \gamma) \end{array} \right. \tag{6.30}$$

Applying the normality rule to all internal state variables, its rates are then defined as

$$\begin{aligned}
\dot{\varepsilon}_{ij}^p &= \dot{\lambda}^p \frac{\partial f_p(\sigma_{ij}, R)}{\partial \sigma_{ij}} + \dot{\lambda}^d \frac{\partial f_d(Y_{ij}, \gamma)}{\partial \sigma_{ij}} = \dot{\lambda}^p \frac{\partial f_p}{\partial \sigma_{ij}} \\
\dot{D}_{ij} &= \dot{\lambda}^p \frac{\partial f_p(\sigma_{ij}, R)}{\partial Y_{ij}} + \dot{\lambda}^d \frac{\partial f_d(Y_{ij}, \gamma)}{\partial Y_{ij}} = \dot{\lambda}^d \frac{\partial f_d}{\partial Y_{ij}} \\
\dot{\sigma} &= \dot{\lambda}^p \frac{\partial f_p(\sigma_{ij}, R)}{\partial \gamma} + \dot{\lambda}^d \frac{\partial f_d(Y_{ij}, \gamma)}{\partial \gamma} = \dot{\lambda}^d \frac{\partial f_d}{\partial \gamma} \\
\dot{p} &= \dot{\lambda}^p \frac{\partial f_p(\sigma_{ij}, R)}{\partial R} + \dot{\lambda}^d \frac{\partial f_d(Y_{ij}, \gamma)}{\partial R} = \dot{\lambda}^p \frac{\partial f_p}{\partial R}
\end{aligned} \tag{6.31}$$

If both yield potential f and surface g are the same the model is said to be associated, otherwise it is called non-associated. The present model considers an associative behavior, so only is necessary to define in detail the surface yield function.

The stress rate can be redefined as function of the Lagrange multipliers when Eq. (6.31) is introduced into Eq. (6.29) as,

$$\dot{\sigma}_{ij} = C_{ijkl} \dot{\varepsilon}_{kl} - C_{ijkl} \frac{\partial f_p}{\partial \sigma_{kl}} \dot{\lambda}^p + \frac{\partial \sigma_{ij}}{\partial D_{kl}} \frac{\partial f_d}{\partial Y_{kl}} \dot{\lambda}^d \tag{6.32}$$

Step 5

Two yield surfaces are defined as the plastic-strain g_p and damage g_d , as

$$\begin{cases} g_p(\sigma_{ij}, R) \\ g_d(Y_{ij}, \gamma) \end{cases} \tag{6.33}$$

The plastic-strain surface is defined as

$$g_p(\sigma_{ij}, R) = \hat{g}_p(\sigma_{ij}) - \hat{R}(R) \tag{6.34}$$

where

$$\begin{cases} \hat{g}_p = \sqrt{\sigma_{ij} f_{ijkl} \sigma_{kl} + f_{ij} \sigma_{ij}} \\ \hat{R} = R(p) + R_0 \end{cases}$$

The yield surface potential is based on the Tsai-Wu failure polynomial, which is an interacting failure criterion since all stress components are used simultaneously to determine whether a failure at a material point has occurred or not. The tensorial expression of the three-dimensional form of the Tsai-Wu failure polynomial is used to define the equivalent state of stresses in the media as define in Eq. (6.31). The values of the polynomial coefficients, f_{ij} and f_{ijkl} , are dependent on the allowable material ultimate strength values as given by

$$\begin{aligned}
f_{11} &= F_1 = \frac{1}{F_{1t}} - \frac{1}{F_{1c}}; & f_{22} &= F_2 = \frac{1}{F_{2t}} - \frac{1}{F_{2c}}; & f_{33} &= F_3 = \frac{1}{F_{3t}} - \frac{1}{F_{3c}} \\
f_{1111} &= F_{11} = \frac{1}{F_{1t} F_{1c}}; & f_{2222} &= F_{22} = \frac{1}{F_{2t} F_{2c}}; & f_{3333} &= F_{33} = \frac{1}{F_{3t} F_{3c}} \\
f_{2233} &= f_{3322} = \frac{1}{2} F_{23} \cong \frac{1}{2} \frac{(-1)}{\sqrt{F_{2t} F_{2c} F_{3t} F_{3c}}} \\
f_{1133} &= f_{3311} = \frac{1}{2} F_{13} \cong \frac{1}{2} \frac{(-1)}{\sqrt{F_{1t} F_{1c} F_{3t} F_{3c}}} \\
f_{1122} &= f_{2211} = \frac{1}{2} F_{12} \cong \frac{1}{2} \frac{(-1)}{\sqrt{F_{1t} F_{1c} F_{2t} F_{2c}}} \\
f_{2323} &= f_{3332} = f_{3223} = f_{3232} = \frac{1}{4} F_{44} = \frac{1}{4} \frac{1}{F_4^2} \\
f_{1313} &= f_{1331} = f_{3113} = f_{3131} = \frac{1}{4} F_{55} = \frac{1}{4} \frac{1}{F_5^2} \\
f_{1212} &= f_{1221} = f_{2112} = f_{2121} = \frac{1}{4} F_{66} = \frac{1}{4} \frac{1}{F_6^2}
\end{aligned} \tag{6.35}$$

The damage surface is defined similarly to the plastic-strain surface, so

$$g_d(Y_{ij}, \gamma) = \hat{g}_d(Y_{ij}) - \hat{\gamma}(\gamma) \tag{6.36}$$

where

$$\begin{cases} \hat{g}_d = \sqrt{Y_{ij}^N j_{ijkl} Y_{kl}^N} + \sqrt{Y_{ij}^S b_{ijkl} Y_{kl}^S} \\ \hat{\gamma} = \gamma(\delta) + \gamma_0 \end{cases}$$

where Y^N and Y^S represent the thermodynamic forces due to normal and shear stresses respectively. The coefficients j_{ijkl} and b_{ijkl} are the tensorial expression of the material properties $J_{11}, J_{22}, J_{33}, B_{11}, B_{22}$, and B_{33} , so

$$\begin{aligned}
j_{1111} &= J_{11}; & j_{2222} &= J_{22}; & j_{3333} &= J_{33} \\
j_{1122} &= j_{2211} = J_{12} \cong \sqrt{J_{11} J_{22}} \\
j_{1133} &= j_{3311} = J_{13} \cong \sqrt{J_{11} J_{33}} \\
j_{2233} &= j_{3322} = J_{23} \cong \sqrt{J_{22} J_{33}} \\
b_{1111} &= B_{11}; & b_{2222} &= B_{22}; & b_{3333} &= B_{33} \\
b_{1122} &= b_{2211} = B_{12} \cong \sqrt{B_{11} B_{22}} \\
b_{1133} &= b_{3311} = B_{13} \cong \sqrt{B_{11} B_{33}}
\end{aligned}$$

$$b_{2233} = b_{3322} = B_{23} \cong \sqrt{B_{22} B_{33}} \quad (6.37)$$

The material properties B_{ii} are those related to the shear components. While J_{ii} is related to the principal directions and takes into account the sense of the strain direction, tension or compression, so

$$J_{ii} = \begin{cases} J_{ii}^t & , \varepsilon_{ii} > 0 \\ J_{ii}^c & , \varepsilon_{ii} < 0 \end{cases} \quad (6.38)$$

Step 6

The consistency conditions will be divided into only plastic, only damage and both damage-plastic evolutions.

a) When no damage is present $\dot{\lambda}^d = 0$, and applying the consistency conditions for plasticity potential only, we have

$$\dot{g}_p = \frac{d g_p(\sigma_{ij}, R)}{dt} = \frac{\partial g_p}{\partial \sigma_{ij}} \dot{\sigma}_{ij} + \frac{\partial g_p}{\partial R} \dot{R} = 0 \quad (6.39)$$

then, after some mathematical manipulation the plastic multiplier is obtained as

$$\begin{aligned} \frac{\partial g_p}{\partial \sigma_{ij}} \left(\frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}} \dot{\varepsilon}_{kl} + \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}^p} \dot{\varepsilon}_{kl}^p + \frac{\partial \sigma_{ij}}{\partial D_{kl}} \dot{D}_{kl} \right) + \frac{\partial g_p}{\partial R} \left(\frac{\partial R}{\partial p} \dot{p} \right) &= 0 \\ \frac{\partial g_p}{\partial \sigma_{ij}} \left(\frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}} \dot{\varepsilon}_{kl} + \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}^p} \dot{\lambda}^p \frac{\partial f_p}{\partial \sigma_{ij}} + \frac{\partial \sigma_{ij}}{\partial D_{kl}} \dot{\lambda}^d \frac{\partial f_d}{\partial Y_{ij}} \right) + \frac{\partial g_p}{\partial R} \left(\frac{\partial R}{\partial p} \dot{\lambda}^p \frac{\partial f_p}{\partial R} \right) &= 0 \\ \left(\frac{\partial g_p}{\partial \sigma_{ij}} \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}^p} \frac{\partial f_p}{\partial \sigma_{ij}} + \frac{\partial g_p}{\partial R} \frac{\partial R}{\partial p} \frac{\partial f_p}{\partial R} \right) \dot{\lambda}^p &= - \frac{\partial g_p}{\partial \sigma_{ij}} \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}} \dot{\varepsilon}_{kl} \\ a_{11} \dot{\lambda}^p &= -b_{kl}^p \dot{\varepsilon}_{kl} \\ \dot{\lambda}^p &= - \frac{b_{kl}^p \dot{\varepsilon}_{kl}}{a_{11}} \\ \dot{\lambda}^p &= L_{kl}^{pp} \dot{\varepsilon}_{kl} \end{aligned} \quad (6.40)$$

Replacing into the stress rate given in Eq. (6.32)

$$\dot{\sigma}_{ij} = \left(C_{ijkl} - C_{ijmn} \frac{\partial f_p}{\partial \sigma_{mn}} L_{kl}^{pp} \right) \dot{\varepsilon}_{kl} \quad (6.33)$$

Since the jacobian is well known expressed as

$$\dot{\sigma}_{ij} = \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}} \dot{\varepsilon}_{kl} \quad (6.34)$$

then the jacobian or elasto-plasto tangent modulus is obtained for the case of only plastic evolution as,

$$\frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}} = C_{ijkl}^e + C_{ijkl}^{pp}, \quad \begin{cases} \dot{\lambda}^p > 0 \\ \dot{\lambda}^d = 0 \end{cases} \quad (6.35)$$

where,

$$\begin{cases} C_{ijkl}^e = C_{ijkl} \\ C_{ijkl}^{pp} = -C_{ijmn} \frac{\partial f_p}{\partial \sigma_{mn}} L_{kl}^{pp} \end{cases}$$

b) When no plasticity is present $\dot{\lambda}^p = 0$, and applying the consistency conditions for damage potential only, we have

$$\dot{g}_d = \frac{dg_d(Y_{ij}, \gamma)}{dt} = \frac{\partial g_d}{\partial Y_{ij}} \dot{Y}_{ij} + \frac{\partial g_d}{\partial \gamma} \dot{\gamma} = 0 \quad (6.36)$$

then, after some mathematical manipulation the damage multiplier is obtained as

$$\begin{aligned} & \frac{\partial g_d}{\partial Y_{ij}} \left(\frac{\partial Y_{ij}}{\partial \varepsilon_{kl}} \dot{\varepsilon}_{kl} + \frac{\partial Y_{ij}}{\partial \varepsilon_{kl}^p} \dot{\varepsilon}_{kl}^p + \frac{\partial Y_{ij}}{\partial D_{kl}} \dot{D}_{kl} \right) + \frac{\partial g_d}{\partial \gamma} \left(\frac{\partial \gamma}{\partial \delta} \dot{\delta} \right) \dot{\gamma} = 0 \\ & \frac{\partial g_d}{\partial Y_{ij}} \left(\frac{\partial Y_{ij}}{\partial \varepsilon_{kl}} \dot{\varepsilon}_{kl} + \frac{\partial Y_{ij}}{\partial \varepsilon_{kl}^p} \dot{\lambda}^p \frac{\partial f_p}{\partial \sigma_{ij}} + \frac{\partial Y_{ij}}{\partial D_{kl}} \dot{\lambda}^d \frac{\partial f_d}{\partial Y_{ij}} \right) + \frac{\partial g_d}{\partial \gamma} \left(\frac{\partial \gamma}{\partial \delta} \dot{\lambda}^d \frac{\partial f_d}{\partial \gamma} \right) = 0 \\ & \left(\frac{\partial g_d}{\partial Y_{ij}} \frac{\partial Y_{ij}}{\partial \varepsilon_{kl}^p} \frac{\partial f_p}{\partial \sigma_{ij}} \right) \dot{\lambda}^p + \left(\frac{\partial g_d}{\partial Y_{ij}} \frac{\partial Y_{ij}}{\partial D_{kl}} \frac{\partial f_d}{\partial Y_{ij}} + \frac{\partial g_d}{\partial \gamma} \frac{\partial \gamma}{\partial \delta} \frac{\partial f_d}{\partial \gamma} \right) \dot{\lambda}^d = - \frac{\partial g_d}{\partial Y_{ij}} \frac{\partial Y_{ij}}{\partial \varepsilon_{kl}} \dot{\varepsilon}_{kl} \\ & a_{22} \dot{\lambda}^d = -b_{kl}^d \dot{\varepsilon}_{kl} \\ & \dot{\lambda}^d = - \frac{b_{kl}^d \dot{\varepsilon}_{kl}}{a_{22}} \\ & \dot{\lambda}^d = L_{kl}^{dd} \dot{\varepsilon}_{kl} \end{aligned} \quad (6.37)$$

Replacing into the stress rate given in Eq. (6.32)

$$\dot{\sigma}_{ij} = \left(C_{ijkl} + \frac{\partial \sigma_{ij}}{\partial D_{mn}} \frac{\partial f_d}{\partial Y_{mn}} L_{kl}^{dd} \right) \dot{\varepsilon}_{kl} \quad (6.38)$$

and comparing it with the Jacobian definition given in Eq. (6.34), then the Jacobian or elasto-damage tangent modulus is obtained for the case of only damage evolution as,

$$\frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}} = C_{ijkl}^e + C_{ijkl}^{dd}, \quad \begin{cases} \dot{\lambda}^p = 0 \\ \dot{\lambda}^d > 0 \end{cases} \quad (6.39)$$

where,

$$\begin{cases} C_{ijkl}^e = C_{ijkl} \\ C_{ijkl}^{dd} = \frac{\partial \sigma_{ij}}{\partial D_{mn}} \frac{\partial f_d}{\partial Y_{mn}} L_{kl}^{dd} \end{cases}$$

c) Applying the consistency conditions for both surface potentials, we have

$$\begin{cases} \dot{g}_p = \frac{\partial g_p}{\partial \sigma_{ij}} \dot{\sigma}_{ij} + \frac{\partial g_p}{\partial R} \dot{R} = 0 \\ \dot{g}_d = \frac{\partial g_d}{\partial Y_{ij}} \dot{Y}_{ij} + \frac{\partial g_d}{\partial \gamma} \dot{\gamma} = 0 \end{cases} \quad (6.40)$$

after using the previous relations, the consistency conditions can be expressed in a matrix form as,

$$\begin{bmatrix} \frac{\partial g_p}{\partial \sigma_{ij}} \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}^p} \frac{\partial f_p}{\partial \sigma_{kl}} + \frac{\partial g_p}{\partial R} \frac{\partial R}{\partial p} \frac{\partial f_p}{\partial R} & \frac{\partial g_p}{\partial \sigma_{ij}} \frac{\partial \sigma_{ij}}{\partial D_{kl}} \frac{\partial f_d}{\partial Y_{kl}} \\ \frac{\partial g_d}{\partial Y_{ij}} \frac{\partial Y_{ij}}{\partial \varepsilon_{kl}^p} \frac{\partial f_p}{\partial \sigma_{kl}} & \frac{\partial g_d}{\partial Y_{ij}} \frac{\partial Y_{ij}}{\partial D_{kl}} \frac{\partial f_d}{\partial Y_{kl}} + \frac{\partial g_d}{\partial \gamma} \frac{\partial \gamma}{\partial \delta} \frac{\partial f_d}{\partial \gamma} \end{bmatrix} \begin{Bmatrix} \dot{\lambda}^p \\ \dot{\lambda}^d \end{Bmatrix} = \begin{Bmatrix} -\frac{\partial g_p}{\partial \sigma_{ij}} \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}} \dot{\varepsilon}_{kl} \\ -\frac{\partial g_d}{\partial Y_{ij}} \frac{\partial Y_{ij}}{\partial \varepsilon_{kl}} \dot{\varepsilon}_{kl} \end{Bmatrix}$$

or,

$$\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \begin{Bmatrix} \dot{\lambda}^p \\ \dot{\lambda}^d \end{Bmatrix} = \begin{Bmatrix} -b_{ij}^p \dot{\varepsilon}_{ij} \\ -b_{ij}^d \dot{\varepsilon}_{ij} \end{Bmatrix}$$

inverting the matrix, a solution for the multipliers is obtained as,

$$\begin{Bmatrix} \dot{\lambda}^p \\ \dot{\lambda}^d \end{Bmatrix} = \frac{1}{a_{11} a_{22} - a_{12} a_{21}} \begin{Bmatrix} a_{12} b_{ij}^d - a_{22} b_{ij}^p \\ a_{21} b_{ij}^p - a_{11} b_{ij}^d \end{Bmatrix} \dot{\varepsilon}_{ij}$$

or, when expressed explicitly

$$\begin{cases} \dot{\lambda}^p = \frac{a_{12}b_{ij}^d - a_{22}b_{ij}^p}{a_{11}a_{22} - a_{12}a_{21}} \dot{\varepsilon}_{ij} = L_{ij}^p \dot{\varepsilon}_{ij} \\ \dot{\lambda}^d = \frac{a_{21}b_{ij}^p - a_{11}b_{ij}^d}{a_{11}a_{22} - a_{12}a_{21}} \dot{\varepsilon}_{ij} = L_{ij}^d \dot{\varepsilon}_{ij} \end{cases} \quad (6.41)$$

Replacing the previous relations into the stress rate,

$$\dot{\sigma}_{ij} = \left(C_{ijkl} - C_{ijmn} \frac{\partial f_p}{\partial \sigma_{mn}} L_{kl}^p + \frac{\partial \sigma_{ij}}{\partial D_{mn}} \frac{\partial f_d}{\partial Y_{mn}} L_{kl}^d \right) \dot{\varepsilon}_{kl} \quad (6.42)$$

then the Jacobian or elasto-plasto-damage tangent modulus is obtained for the case of plastic and damage evolution as,

$$\frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}} = C_{ijkl}^e + C_{ijkl}^p + C_{ijkl}^d, \quad \begin{cases} \dot{\lambda}^p > 0 \\ \dot{\lambda}^d > 0 \end{cases} \quad (6.39)$$

where,

$$\begin{cases} C_{ijkl}^e = C_{ijkl} \\ C_{ijkl}^{pp} = -C_{ijmn} \frac{\partial f_p}{\partial \sigma_{mn}} L_{kl}^p \\ C_{ijkl}^{dp} = \frac{\partial \sigma_{ij}}{\partial D_{mn}} \frac{\partial f_d}{\partial Y_{mn}} L_{kl}^d \end{cases}$$

Step 7

A plastic behavior is expected when the yield surface is positive, $g > 0$, or the state of stresses exceeds the yield boundary when the total strain has reached a new value. At this point the Lagrange multiplier is zero, point C' in Figure 6-8, but the equilibrium will be reached when the yield surface leads to zero, $g = 0$ for the same total strain. At this point, C , the Lagrangian multiplier is bigger than zero.

As it can be seen, the new value of the Lagrangian multiplier can be solved when the yield surface function is zero. Since this surface function can be obtained parametrically from the Lagrangian multiplier, then the root of the function can be obtained using the Newton method, which is an iterative method where each step is defined as a function of the previous as,

$$\dot{\lambda}_k = \dot{\lambda}_{k-1} - \frac{g|_{k-1}}{\frac{dg}{d\dot{\lambda}}|_{k-1}} \quad (6.40)$$

Figure 6-8 Discretization of the Lagrange multiplier evolution

Since no variation in the total strain is expected for the actual time step $()^n$, by definition, the partial derivative of this total strain with respect either of the plastic or damage multipliers are zero, then for

$$\varepsilon_{ij} = (\varepsilon_{ij})^n \quad \Rightarrow \quad \frac{\partial \varepsilon_{ij}}{\partial \dot{\lambda}^p} = \frac{\partial \varepsilon_{ij}}{\partial \dot{\lambda}^d} = 0 \quad (6.41)$$

From the rate of the internal variables given in Eq. (6.31), the following relations are derived as,

$$\begin{aligned} \frac{\partial \varepsilon_{ij}^p}{\partial \dot{\lambda}^p} &= \frac{\partial f_p}{\partial \sigma_{ij}} \\ \frac{\partial D_{ij}}{\partial \dot{\lambda}^d} &= \frac{\partial f_d}{\partial Y_{ij}} \\ \frac{\partial \delta}{\partial \dot{\lambda}^d} &= \frac{\partial f_d}{\partial \gamma} \\ \frac{\partial p}{\partial \dot{\lambda}^p} &= \frac{\partial f_p}{\partial R} \end{aligned} \quad (6.42)$$

and also,

$$\frac{\partial \varepsilon_{ij}^p}{\partial \dot{\lambda}^d} = \frac{\partial D_{ij}}{\partial \dot{\lambda}^p} = \frac{\partial \delta}{\partial \dot{\lambda}^p} = \frac{\partial p}{\partial \dot{\lambda}^d} = 0 \quad (6.43)$$

The derivative of the plastic and damage surfaces with respect to the plastic and damage Lagrangian multipliers are obtained using the relations in Eqs. (6.41) to (6.43) as,

$$\begin{aligned}
\frac{dg_p}{d\dot{\lambda}^p} &= \frac{dg_p(\sigma_{ij}, R)}{d\dot{\lambda}^p} = \frac{\partial g_p}{\partial \sigma_{ij}} \frac{\partial \sigma_{ij}}{\partial \dot{\lambda}^p} + \frac{\partial g_p}{\partial R} \frac{\partial R}{\partial \dot{\lambda}^p} \\
&= \frac{\partial g_p}{\partial \sigma_{ij}} \frac{\partial \sigma_{ij}(\varepsilon_{ij}, \varepsilon_{ij}^p, D_{ij})}{\partial \dot{\lambda}^p} + \frac{\partial g_p}{\partial R} \frac{\partial R(p)}{\partial \dot{\lambda}^p} \\
&= \frac{\partial g_p}{\partial \sigma_{ij}} \left[\frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}} \frac{\partial \varepsilon_{kl}}{\partial \dot{\lambda}^p} + \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}^p} \frac{\partial \varepsilon_{kl}^p}{\partial \dot{\lambda}^p} + \frac{\partial \sigma_{ij}}{\partial D_{kl}} \frac{\partial D_{kl}}{\partial \dot{\lambda}^p} \right] + \frac{\partial g_p}{\partial R} \frac{\partial R}{\partial p} \frac{\partial p}{\partial \dot{\lambda}^p} \\
&= \frac{\partial g_p}{\partial \sigma_{ij}} \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}^p} \frac{\partial f_p}{\partial \sigma_{ij}} + \frac{\partial g_p}{\partial R} \frac{\partial R}{\partial p} \frac{\partial f_p}{\partial R} \\
\frac{dg_p}{d\dot{\lambda}^p} &= a_{11}
\end{aligned} \tag{6.41}$$

$$\begin{aligned}
\frac{\partial g_p}{\partial \dot{\lambda}^d} &= \frac{\partial g_p(\sigma_{ij}, R)}{\partial \dot{\lambda}^d} = \frac{\partial g_p}{\partial \sigma_{ij}} \frac{\partial \sigma_{ij}}{\partial \dot{\lambda}^d} + \frac{\partial g_p}{\partial R} \frac{\partial R}{\partial \dot{\lambda}^d} \\
&= \frac{\partial g_p}{\partial \sigma_{ij}} \frac{\partial \sigma_{ij}(\varepsilon_{ij}, \varepsilon_{ij}^p, D_{ij})}{\partial \dot{\lambda}^d} + \frac{\partial g_p}{\partial R} \frac{\partial R(p)}{\partial \dot{\lambda}^d} \\
&= \frac{\partial g_p}{\partial \sigma_{ij}} \left[\frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}} \frac{\partial \varepsilon_{kl}}{\partial \dot{\lambda}^d} + \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}^p} \frac{\partial \varepsilon_{kl}^p}{\partial \dot{\lambda}^d} + \frac{\partial \sigma_{ij}}{\partial D_{kl}} \frac{\partial D_{kl}}{\partial \dot{\lambda}^d} \right] + \frac{\partial g_p}{\partial R} \frac{\partial R}{\partial p} \frac{\partial p}{\partial \dot{\lambda}^d} \\
&= \frac{\partial g_p}{\partial \sigma_{ij}} \frac{\partial \sigma_{ij}}{\partial D_{kl}} \frac{\partial f_d}{\partial Y_{ij}} \\
\frac{\partial g_p}{\partial \dot{\lambda}^d} &= a_{12}
\end{aligned} \tag{6.41}$$

$$\begin{aligned}
\frac{\partial g_d}{\partial \dot{\lambda}^d} &= \frac{\partial g_d(Y_{ij}, \gamma)}{\partial \dot{\lambda}^d} = \frac{\partial g_d}{\partial Y_{ij}} \frac{\partial Y_{ij}}{\partial \dot{\lambda}^d} + \frac{\partial g_d}{\partial \gamma} \frac{\partial \gamma}{\partial \dot{\lambda}^d} \\
&= \frac{\partial g_d}{\partial Y_{ij}} \frac{\partial Y_{ij}(\varepsilon_{ij}, \varepsilon_{ij}^p, D_{ij})}{\partial \dot{\lambda}^d} + \frac{\partial g_d}{\partial \gamma} \frac{\partial \gamma(\delta)}{\partial \dot{\lambda}^d} \\
&= \frac{\partial g_d}{\partial Y_{ij}} \left[\frac{\partial Y_{ij}}{\partial \varepsilon_{kl}} \frac{\partial \varepsilon_{kl}}{\partial \dot{\lambda}^d} + \frac{\partial Y_{ij}}{\partial \varepsilon_{kl}^p} \frac{\partial \varepsilon_{kl}^p}{\partial \dot{\lambda}^d} + \frac{\partial Y_{ij}}{\partial D_{kl}} \frac{\partial D_{kl}}{\partial \dot{\lambda}^d} \right] + \frac{\partial g_d}{\partial \gamma} \frac{\partial \gamma}{\partial \delta} \frac{\partial \delta}{\partial \dot{\lambda}^d} \\
&= \frac{\partial g_d}{\partial Y_{ij}} \frac{\partial Y_{ij}}{\partial D_{kl}} \frac{\partial f_d}{\partial Y_{ij}} + \frac{\partial g_d}{\partial \gamma} \frac{\partial R}{\partial p} \frac{\partial f_d}{\partial \gamma} \\
\frac{\partial g_d}{\partial \dot{\lambda}^d} &= a_{22}
\end{aligned} \tag{6.41}$$

$$\begin{aligned}
\frac{\partial g_d}{\partial \dot{\lambda}^p} &= \frac{\partial g_d(Y_{ij}, \gamma)}{\partial \dot{\lambda}^p} = \frac{\partial g_d}{\partial Y_{ij}} \frac{\partial Y_{ij}}{\partial \dot{\lambda}^p} + \frac{\partial g_d}{\partial \gamma} \frac{\partial \gamma}{\partial \dot{\lambda}^p} \\
&= \frac{\partial g_d}{\partial Y_{ij}} \frac{\partial Y_{ij}(\varepsilon_{ij}, \varepsilon_{ij}^p, D_{ij})}{\partial \dot{\lambda}^p} + \frac{\partial g_d}{\partial \gamma} \frac{\partial \gamma(\delta)}{\partial \dot{\lambda}^p} \\
&= \frac{\partial g_d}{\partial Y_{ij}} \left[\frac{\partial Y_{ij}}{\partial \varepsilon_{kl}} \frac{\partial \varepsilon_{kl}}{\partial \dot{\lambda}^p} + \frac{\partial Y_{ij}}{\partial \varepsilon_{kl}^p} \frac{\partial \varepsilon_{kl}^p}{\partial \dot{\lambda}^p} + \frac{\partial Y_{ij}}{\partial D_{kl}} \frac{\partial D_{kl}}{\partial \dot{\lambda}^p} \right] + \frac{\partial g_d}{\partial \gamma} \frac{\partial \gamma}{\partial \delta} \frac{\partial \delta}{\partial \dot{\lambda}^p} \\
&= \frac{\partial g_d}{\partial Y_{ij}} \frac{\partial Y_{ij}}{\partial \varepsilon_{kl}^p} \frac{\partial f_p}{\partial \sigma_{kl}} \\
\frac{\partial g_d}{\partial \dot{\lambda}^p} &= a_{21}
\end{aligned} \tag{6.41}$$

When an associated formulation is considered, the discretization of the internal variables is obtained from the rate of internal variables as,

$$\begin{aligned}
\dot{\varepsilon}_{ij}^p &= \dot{\lambda}^p \frac{\partial f_p}{\partial \sigma_{ij}} \quad \Rightarrow \quad (\varepsilon_{ij}^p)_k^n = (\varepsilon_{ij}^p)_k^{n-1} + \dot{\lambda}_k^p \left(\frac{\partial f_p}{\partial \sigma_{ij}} \right)_k^n = (\varepsilon_{ij}^p)_k^{n-1} + \dot{\lambda}_k^p \left(\frac{\partial g_p}{\partial \sigma_{ij}} \right)_k^n \\
\dot{p} &= \dot{\lambda}^p \frac{\partial f_p}{\partial R} \quad \Rightarrow \quad (p)_k^n = (p)_k^{n-1} + \dot{\lambda}_k^p \left(\frac{\partial f_p}{\partial R} \right)_k^n = (p)_k^{n-1} + \dot{\lambda}_k^p \\
\dot{D}_{ij} &= \dot{\lambda}^d \frac{\partial f_d}{\partial Y_{ij}} \quad \Rightarrow \quad (D_{ij})_k^n = (D_{ij})_k^{n-1} + \dot{\lambda}_k^d \left(\frac{\partial f_d}{\partial Y_{ij}} \right)_k^n = (D_{ij})_k^{n-1} + \dot{\lambda}_k^d \left(\frac{\partial g_d}{\partial Y_{ij}} \right)_k^n \\
\dot{\delta} &= \dot{\lambda}^d \frac{\partial f_d}{\partial \gamma} \quad \Rightarrow \quad (\delta)_k^n = (\delta)_k^{n-1} + \dot{\lambda}_k^d \left(\frac{\partial f_d}{\partial \gamma} \right)_k^n = (\delta)_k^{n-1} + \dot{\lambda}_k^d
\end{aligned} \tag{6.42}$$

The previous formulations are used to define the evolution of the discrete Lagrange multipliers which will converge to values that make true the consistency conditions or make the yield or damage functions become zero.

a) For the case of only plastic evolution, the Newton Rhapsion iteration method is defined as,

$$\dot{\lambda}_k^p = \dot{\lambda}_{k-1}^p - \frac{g_p|_{k-1}}{\frac{dg_p}{d\dot{\lambda}^p}|_{k-1}} \tag{6.41}$$

and finally the discretization of the Lagrange multiplier evolution is then obtained as,

$$\dot{\lambda}_k^p = \dot{\lambda}_{k-1}^p - \frac{(g_p)_{k-1}^n}{(a_{11})_{k-1}^n} \quad (6.42)$$

b) For the case of only damage evolution, the Newton Rhapson iteration method is defined as,

$$\dot{\lambda}_k^d = \dot{\lambda}_{k-1}^d - \frac{g_d|_{k-1}}{\left. \frac{dg_d}{d\dot{\lambda}^d} \right|_{k-1}} \quad (6.43)$$

and its discretization of the Lagrange damage multiplier evolution is obtained as,

$$\dot{\lambda}_k^d = \dot{\lambda}_{k-1}^d - \frac{(g_d)_{k-1}^n}{(a_{22})_{k-1}^n} \quad (6.44)$$

c) For the case of both plastic and damage evolution, the Newton Rhapson iteration method is defined using a Jacobian matrix defined as,

$$\begin{bmatrix} \frac{\partial g_p}{\partial \dot{\lambda}^p} & \frac{\partial g_p}{\partial \dot{\lambda}^d} \\ \frac{\partial g_d}{\partial \dot{\lambda}^p} & \frac{\partial g_d}{\partial \dot{\lambda}^d} \end{bmatrix}_{k-1} \begin{Bmatrix} \dot{\lambda}_k^p - \dot{\lambda}_{k-1}^p \\ \dot{\lambda}_k^d - \dot{\lambda}_{k-1}^d \end{Bmatrix} = - \begin{Bmatrix} g_p \\ g_d \end{Bmatrix}_{k-1} \quad (6.44)$$

and the discretization of both plastic and damage Lagrange multipliers are obtained as,

$$\begin{bmatrix} (a_{11})_{k-1}^n & (a_{12})_{k-1}^n \\ (a_{21})_{k-1}^n & (a_{22})_{k-1}^n \end{bmatrix} \begin{Bmatrix} \dot{\lambda}_k^p - \dot{\lambda}_{k-1}^p \\ \dot{\lambda}_k^d - \dot{\lambda}_{k-1}^d \end{Bmatrix} = - \begin{Bmatrix} (g_p)_{k-1}^n \\ (g_d)_{k-1}^n \end{Bmatrix}$$

then,

$$\begin{cases} \dot{\lambda}_k^p = \dot{\lambda}_{k-1}^p - \frac{(a_{22})_{k-1}^n (g_p)_{k-1}^n - (a_{12})_{k-1}^n (g_d)_{k-1}^n}{(a_{11})_{k-1}^n (a_{22})_{k-1}^n - (a_{12})_{k-1}^n (a_{21})_{k-1}^n} \\ \dot{\lambda}_k^d = \dot{\lambda}_{k-1}^d - \frac{(a_{11})_{k-1}^n (g_d)_{k-1}^n - (a_{21})_{k-1}^n (g_p)_{k-1}^n}{(a_{11})_{k-1}^n (a_{22})_{k-1}^n - (a_{12})_{k-1}^n (a_{21})_{k-1}^n} \end{cases} \quad (6.45)$$

6.6 Material parameters evaluation

The material parameters used to define the plastic yield surface are well known as the strength failure values. These plastic parameters are defined in Eq. (6.35) and included in the Tsai-Wu failure coefficients. By the other hand, no parameters are available in the literature for the coefficients of the damage surface, expressed in Eq. (6.37)

Also the coefficients that define the plastic or damage evolution, expressed in Eqs. (6.25c) and (6.25d) respectively, considering in this case Prony series are not known for either case. The proposed method to find these coefficients starts with an experimental stress strain data where load and unload loading have been performed to the probe, as seen in Figure 6-9.

Figure 6-9 Stress- strain load unload available data.

Important information is obtained directly from this strain stress curve, where the information will depend on the type of loading done onto the specimen, tension, compression, shear and the applied load direction with respect to the material coordinates 1, 2 or 3. The initial or undamaged stiffness $\bar{E}_{ij}$, the final, ultimate, or critical stiffness $\tilde{E}_{ij}$, the ultimate strength F_{ij} , the limit linear strength $S_{ij,Linear}$, the final, ultimate, or critical total strain $\tilde{\epsilon}_{ij}$, and the critical, ultimate, or final plastic strain $\tilde{\epsilon}_{ij}^p$. A fitted stress strain curve can also be evaluated.

When the strain vs. plastic strain is plotted using the available data, the strain damage threshold can be obtained after the points are fitted. Where this fitted function intersects

the strain axes the strain threshold is defined. In Figure 6-10(a) this fitted curve is represented as a line, but it could have any shape, concave or convex.

Figure 6-10 Plastic and damage strain threshold.

In an analogous manner the strain damage threshold can be found. The main difference is that the strain threshold is defined when the fitted curve intersects the undamaged stiffness. This threshold values can now be plotted in the strain stress curve, as seen in Figure 6-11. Using the fitted strain stress curve obtained for Figure 6-9, strength threshold values can be obtained for plastic and damage behaviors.

Figure 6-11 Plastic and damage stress threshold.

It is important to notice that not necessarily the threshold values for plasticity and damage will be the same. Experimental data suggests that usually plasticity have bigger values, where this depends on the material evaluated. In some few cases damage threshold values where bigger.

Considering an associative behavior and since the Lagrangian multiplier is the same for the isotropic plastic evolution and plastic strain ratios, then a relation of these rates can be expressed as

$$\begin{cases} \dot{p} = \dot{\lambda}^p \frac{\partial f_p}{\partial R} \\ \dot{\varepsilon}_{ij}^p = \dot{\lambda}^p \frac{\partial f_p}{\partial \sigma_{ij}} \end{cases} \Rightarrow \dot{p} = - \frac{\dot{\varepsilon}_{ij}^p}{\frac{\partial g_p}{\partial \sigma_{ij}}} \quad (6.46)$$

Since the partial derivate of the plastic surface w.r.t. the stress is independent of the plastic strain and the isotropic plastic evolution, and since at the beginning of the integration time $t=0$, $\varepsilon_{ij}^p = 0$ and $p=0$, then after performing the integration of Eq. (6.46) a relation between these two internal variables can be expressed

$$p = - \frac{\varepsilon_{ij}^p}{\frac{\partial g_p}{\partial \sigma_{ij}}} \quad (6.47)$$

Starting with a plastic strain stress plot of the available data a plot of the isotropic plastic evolution stress can be done using Eq. (6.47), as seen in Figure 6-12. In this plot is seen that the plastic surface is define for $g_p = 0$ with boundaries at $p=0$ and $p=\tilde{p}$, so

$$g_p = \hat{g}_p - \hat{R} = \hat{g}_p - (R + R_0) = 0 \Rightarrow \hat{g}_p(\sigma_{ij}) - [R(p) + R_0] = 0 \quad (6.48)$$

Figure 6-12 Plastic surface fitting given available data.

Finally, after fitting the data and using the boundary conditions, all material properties and Prony coefficients can be obtained for plastic evolution.

Similar procedure is used when damage is analyzed. First a relation between damage and isotropic damage is obtained as

$$\delta = -\frac{D_{ij}}{\frac{\partial g_d}{\partial Y_{ij}}} \quad (6.49)$$

Since the thermodynamic damage force can be obtained from the state of stresses and having a relation between damaged stiffness with damage and this with the isotropic damage evolution, then a plot of the available data can be obtained as seen in Figure 6-13. The damage surface is obtained for $g_d \neq 0$, so

$$g_d = \hat{g}_d - \hat{\gamma} = \hat{g}_p - (\gamma + \gamma_0) = 0 \quad \Rightarrow \quad \hat{g}_d(Y_{ij}(\sigma_{ij})) - [\gamma(\delta) + \gamma_0] = 0 \quad (6.50)$$

Figure 6-13 Damage surface fitting given available data.

With the use of the boundary conditions seen in Figure 6-13(b) fitting the curve for $g_d = 0$, the damage Prony coefficients and material damage properties can be obtained when comparing it with Eq. (6.50).

A complete plasticity-damage model has been developed in detail. This model can be implemented in a finite element code, which can be used to predict more accurately failure in directional fiber composites, which was the main objective of this point.

This tool will improve the uncertainty of future designs, which increases the security of new developments.

The work presented in this report summarizes the current state-of-the-art in on-board storage on compressed gaseous hydrogen as well as the development of analysis tools, methods, and theoretical data for devising high performance design configurations for hydrogen storage. The state-of-the-art in the area of compressed hydrogen storage reveals that the current configuration of the hydrogen storage tank is a seamless cylindrical part with two end domes. The tank is composed of an aluminum liner overwrapped with carbon fibers. Such a configuration was proved to sustain internal pressures up to 350 bars (5,000 psi).

Finite-element stress analyses were performed on filament-wound hydrogen storage cylindrical tanks under the effect of internal pressure of 700 bars (10,000 psi). Tank deformations, stress fields, and intensities induced at the tank wall were examined. The results indicated that the aluminum liner can not sustain such a high pressure and initiate the tank failure. Thus, hydrogen tanks ought to be built entirely out of composite materials based on carbon fibers or other innovative composite materials.

A spherical hydrogen storage tank was suggested within the scope of this project. A stress reduction was achieved by this change of the tank geometry, which allows for increasing the amount of the stored hydrogen and storage energy density.

The finite element modeling of both cylindrical and spherical tank design configurations indicate that the formation of stress concentration zones in the vicinity of the valve inlet as well as the presence of high shear stresses in this area. Therefore, it is highly recommended to tailor the tank wall design to be thicker in this region and tapered to the required thickness in the rest of the tank shell.

Innovative layout configurations of multiple tanks for enhanced conformability in limited space have been proposed and theoretically modeled using 3D finite element analysis. Optimum tailoring of fiber orientations and lay-ups are needed to relieve the high stress in regions of high stress concentrations between intersecting tanks/ tank sections.

Filament winding process is the most suitable way for producing both cylindrical and spherical hydrogen storage tanks with high industrial quality. However, due to the unavailability of such equipment at West Virginia University and limited funding, the composite structures within this work were produced by hand layup and bag molding techniques. More advanced manufacturing processes can significantly increase the

structural strength of the tank and enhances its performance and also further increase weight saving capabilities.

The concept of using a carbon composite liner seems to be promising in overcoming the low strength of the aluminum liner at internal high pressures. This could be further enhanced by using MetPreg filament winding to produce such a liner.

Innovative designs for the polar boss of the storage tanks and the valve connections are still needed to reduce the high stress formed in these zones to allow for the tank to accommodate higher internal pressures.

The Continuum Damage Mechanics (CDM) approach was applied for fault-tolerant design and efficient maintenance of lightweight automotive structures made of composite materials. Potential effects of damage initiation and accumulation are formulated for various design configurations, with emphasis on lightweight fiber-reinforced composites. The CDM model considers damage associated with plasticity and fatigue.

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