STP-PT-017

PROPERTIES FOR COMPOSITE MATERIALS IN HYDROGEN SERVICE

ASME STANDARDS
TECHNOLOGY, LLC

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Prepared by:

Craig Webster, P.Eng.
Powertech Labs Inc.

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ASME Standards Technology, LLC
Three Park Avenue, New York, NY 10016-5990

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

FOREWORD

Commercialization of hydrogen fuel cells, in particular fuel cell vehicles, will require development of an extensive hydrogen infrastructure comparable to that which exists today for petroleum. This infrastructure must include the means to safely and efficiently generate, transport, distribute, store and use hydrogen as a fuel. Standardization of pressure retaining components, such as tanks, piping and pipelines, will enable hydrogen infrastructure development by establishing confidence in the technical integrity of products.

Since 1884, the American Society of Mechanical Engineers (ASME) has been developing codes and standards (C&S) that protect public health and safety. The traditional approach to standards development involved writing prescriptive standards only after technology has been established and commercialized. With the push toward a hydrogen economy, government and industry have realized that they cannot afford a hydrogen-related safety incident that may undermine consumer confidence. As a result, ASME has adopted a more anticipatory approach to standardization for hydrogen infrastructure which involves writing standards with more performance based requirements in parallel with technology development and before commercialization has begun.

Today, ASME codes and standards are used for hydrogen storage, transmission and distribution. The anticipated requirements of the hydrogen economy will require local refueling stations with the capability to fill gaseous hydrogen vehicle tanks rapidly to pressures as high as 15,000 psig (100 MPa). Although current standards could be used to build pressure tanks, piping and pipelines meeting these operating requirements, it is likely that the resulting components would not, as a practical matter, enable commercialization of the technology.

ASME has worked closely with the Department of Energy (DOE), national laboratories and other standards developing organizations (SDOs) to identify lead organizations to address the need for standards for hydrogen applications. ASME was selected to lead the efforts for pressure tanks, piping and pipelines for storage, transportation and distribution of hydrogen. Initial work of the ASME Hydrogen Steering Committee led to the formation of volunteer task forces under the ASME Board on Pressure Technology Codes and Standards (BPTCS) to explore the standardization requirements for storage tanks, transportation tanks, portable tanks, piping and pipelines for hydrogen-specific applications. The task forces submitted their recommendations at the end of 2003 and these recommendations led to initiation of standards actions, formation of project teams and commencement of supporting research.

The ASME Boiler and Pressure Vessel (BPV) Standards Committee appointed a project team to develop new Code rules in the Boiler and Pressure Vessel Code Section VIII (pressure vessels) and Section XII (transport tanks) for hydrogen storage and transport tanks to be used in the storage and transport of liquid and gaseous hydrogen and metal hydrides. Rules for gaseous storage tanks with maximum allowable working pressures (MAWPs) up to 15,000 psig (100 MPa) will be needed. Research activities are being coordinated to develop data and technical reports concurrent with standards development and have been prioritized per Project Team needs. The Project Team may identify additional needs and gaps as drafts are developed.

The Technical Reports to be developed will establish data and other information to be used to support and facilitate separate initiatives to develop ASME standards for the hydrogen infrastructure. These reports will target specific disciplines and fill the gaps identified by ASME's hydrogen task forces. An initial report, developed under the sponsorship of the National Renewable Energy Laboratory (NREL), Hydrogen Standardization Interim Report for Tanks, Piping and Pipelines was issued on May 3, 2005. This interim report addressed priority topical areas within each of the four pressure technology applications for hydrogen infrastructure development: storage (stationary) tanks, transport tanks, piping and pipelines and vehicle fuel tanks.

The present report builds on the work of the interim report and investigates properties of composite materials in hydrogen service.

Established in 1880, the American Society of Mechanical Engineers (ASME) is a professional not-for-profit organization with more than 127,000 members promoting the art, science and practice of mechanical and multidisciplinary engineering and allied sciences. ASME develops codes and standards that enhance public safety, and provides lifelong learning and technical exchange opportunities benefiting the engineering and technology community. Visit www.asme.org for more information.

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ABSTRACT

Studies were conducted to address three specific questions related to the use of composite-reinforced pressure vessel designs for the transportation of compressed hydrogen at pressures up to 103 MPa (15,000 psi). These studies involved determining the hydrogen embrittlement resistance of AA6061-T6 aluminum alloy material typically used as a liner in composite-reinforced cylinder designs; determining whether composite-reinforced pressure vessels using plastic or thin-wall metallic liners were subject to distortion during the filament winding process; and identifying test methods that can be used to establish the long-term performance of non-metallic materials exposed to high-pressure hydrogen environments.

Long-term hydrogen embrittlement tests were conducted on AA6061-T6 samples using compact tension specimens according to ISO 11114-4, Method C. Specimens were fatigue pre-cracked, following which the fatigue cracks were pre-loaded to various stress intensity factors. The specimens were then inserted into a pressure vessel containing hydrogen at 103 MPa (15,000 psi). After 1,000 hours exposure, there was no evidence observed of any hydrogen-induced crack growth in the aluminum.

A variety of composite-reinforced pressure vessels that use plastic liners and thin-walled aluminum liners, and having lengths up to 3058 mm, were inspected. There was no evidence of any axial distortion. In addition, pressure cycle and burst test data between composite-reinforced pressure vessels of relatively short length and relatively long length were compared, confirming that the designs of different length had the same performance.

Plastic liner materials cut from four high-pressure hydrogen storage tanks of different design were tested for effects of high-temperature ageing and of long-term exposure to high-pressure hydrogen. Specimens were tensile tested in the as-received condition, after one-month exposure to 70 MPa (10,000 psi) hydrogen and after one-month exposure to 85˚C atmosphere. The 70 MPa hydrogen exposure for 30 days had no noticeable effect on the strength of the materials but did create some bubbles in the surface. On average, ageing three of the materials for 30 days at 85˚C caused an increase in tensile strength. It was concluded that more samples needed to be tested to develop a more acceptable statistic average of the mechanical properties, and that full-scale testing should be performed on complete pressure vessels at both high and low service temperatures with hydrogen pressure.

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1 PURPOSE AND USE

This report is intended to answer three specific questions related to the use of specific materials and composite-reinforced pressure vessel designs for the transportation of compressed hydrogen at pressures up to 103 MPa (15,000 psi). The individual studies involve:

- Determining the propensity for hydrogen embrittlement to occur in AA6061-T6 aluminum alloy material typically used as a liner in composite-reinforced cylinder designs.
- Determining whether the manufacture of composite-reinforced pressure vessels of relatively long length over thin-wall metallic liners or plastic liners can result in sagging of the vessels, thus affecting the tension in the filament winding process.
- Identifying test methods that can be used to establish the long-term performance of non-metallic materials exposed to high-pressure hydrogen environments.

2 HYDROGEN EMBRITTLEMENT RESISTANCE OF AA6061-T6 AT 103 MPA (15,000 PSI)

2.1 Summary

Long-term hydrogen embrittlement tests were conducted according to ISO 11114-4, Method C [1]. Compact tension (CT) specimens were withdrawn from the sidewall of a 6061-T6 aluminum alloy cylinder liner. Four samples were machined from the material with the direction of crack propagation longitudinal to the cylinder liner axis. Each specimen was fatigue pre-cracked and then a pin was inserted into a tapered hole to impart a stress intensity of 21.4 MPa-√m for 6061-T6. After loading, the specimens were placed in a cylinder and pressurized to 103 MPa (15,000 psi) with 100% hydrogen.

After 1000 hours of exposure, the samples were visually examined for obvious signs of crack propagation. To ensure that the crack mouth opening displacement (CMOD) had not changed drastically during the test, their values were measured and corresponding stress intensities were calculated. Since crack extension was not visible, the specimens were cyclically loaded to create fatigue striations, marking the end of any hydrogen induced crack propagation. After breaking apart the specimens, it was determined that the cracks did not propagate any further. This was confirmed by taking high magnification micrographs with a scanning electron microscope (SEM).

2.2 Applicable Standards

The test was performed according to Method C of ISO 11114-4, “Transportable Gas Cylinders–Compatibility of Cylinder and Valve Materials with Gas Contents–Part 4: Test Methods for Selecting Metallic Material Resistant to Hydrogen Embrittlement.” Specimen dimensions and the fatigue pre-cracking procedure were taken from ISO 7539-6, “Corrosion of Metals and Alloys–Stress Corrosion Testing” [2] and ASTM E1820-01, “Standard Test Method for Measurement of Fracture Toughness” [3].

2.3 Material

2.3.1 Chemistry

The 6061-T6 aluminum alloy was removed from the liner of a hoop-wrapped cylinder manufactured by the CNG Cylinder Co. The design chemistry is described in Table 1.

Table 1 - Chemistry of Aluminum Alloy 6061 (ASTM B210)

Element	Min (%)	Max (%)
Mg	0.8	1.2
Si	0.4	0.8
Cu	0.15	0.4
Cr	0.04	0.35
Ti	-	0.15
Fe	-	0.7
Mn	-	0.15
Zn	-	0.25