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EFFECT OF HIGH-PRESSURE HYDROGEN AND WATER IMPURITY ON ALUMINUM ALLOYS

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ABSTRACT

Aluminum alloys are desirable in mobile fuel cell applications due to the combination of strength, hydrogen resistance, and low density. In dry hydrogen environments, the fatigue and fracture resistance of common structural aluminum alloys are not degraded compared to air environments. However, aluminum alloys can be susceptible to stress corrosion cracking in humid air, which raises questions about the potential deleterious effects of moisture impurities in high-pressure hydrogen environments. While this study does not address the effects of the air environment on aluminum hydrogen pressure components, we assess the fracture resistance of aluminum alloys in high-pressure hydrogen containing known amount of water. High-pressure gaseous hydrogen at pressure up to 100 MPa is shown to have no effect on elastic-plastic fracture measurements of common high-strength aluminum alloys in tempers designed for resistance to stress corrosion cracking. Complementary sustained load cracking tests in high-pressure hydrogen were also performed in gaseous hydrogen at pressure of approximately 100 MPa with water content near the maximum allowed in hydrogen standards for fuel cell vehicles. These tests show no evidence of environmental-assisted cracking at loading conditions approaching the onset of unstable fracture in this configuration. In summary, typical moisture content in fuel cell grade hydrogen (<5 ppm) do not promote hydrogen-assisted fracture or stress corrosion cracking in the tested aluminum alloys.

INTRODUCTION

Aluminum alloys have appealing properties for vehicle applications, in particular high specific strength. However, many high-strength aluminum alloys are susceptible to stress corrosion cracking, which is attributed to hydrogen embrittlement as a consequence of exposure to water vapor [1-3]. Wei et al. studied the fatigue crack growth rate of a 2219-T851 in air and vacuum, showing a clear dependency on humidity [2]. Their results confirmed the suggestion by Bradshaw and Wheeler that the enhanced crack growth is a function of water vapor and reaction time [3]. On the other hand, tests in low-pressure 'dry' hydrogen show no susceptibility to hydrogen embrittlement [1], suggesting the importance of humidity.

In fuel cell vehicle applications, gaseous hydrogen fuel is stored at high pressure (up to 70 MPa). Fuel cell grade hydrogen allows for up to 5 ppm water impurity in the hydrogen. While this water content is relatively low on a parts per million basis, the partial pressure is significant. In this study, sustained load cracking of several high-strength aluminum alloys is explored in high-pressure gaseous hydrogen with known amount of water vapor. Constant displacement fracture tests were conducted in gaseous hydrogen at pressure of 100 MPa for 1000 hours and the water content of the gas was evaluated at the beginning and conclusion of the tests.

EXPERIMENTAL PROCEDURES

Three high-strength aluminum alloys were considered in this study: two 7000-series alloys (Al-Zn-Mg-Cu) and one 2000-series alloy (Al-Cu). The composition of the alloys is provided

in Table 1. All three alloys were obtained as 76 mm thick plate. Both the 7050 and 7475 alloys were provided in commercial stress relieved and overaged tempers for resistance to stress corrosion cracking (T7X51, as shown in Table 1). The 2219 alloy was supplied in standard stress relieved and artificially aged condition (T851). The tensile properties of the materials are shown in Table 2.

Constant displacement fracture threshold tests were conducted following the procedures in ASTM E1681 and consistent with the methods outlined in HPIS E103. The modified bolt-load compact specimen was used for these tests; this specimen is also commonly referred to as the wedge-opening load (WOL) specimen. The thickness (B) of the specimens was 22.3 mm and the width (W) was 56.9 mm; other dimension were consistent with ASTM E1681. Side grooves reduced the net-section thickness (B_N) to 18.7 mm to ensure uniform crack fronts. The specimens were precracked in air under conditions of load shedding to a nominal crack length (a_o) of 34 mm and K_{max} of 8 MPa $m^{1/2}$ at the conclusion of precracking. The crack location was determined from compliance measurements (and verified optically on the fracture surfaces at the conclusion of testing).

Prior to loading the specimens for environmental testing, one specimen of each material was monotonically loaded in a hydraulic test machine until the precrack propagated and the load dropped while measuring the crack opening displacement at the front face of the specimen. This measurement enabled the determination of a critical crack opening displacement (and stress intensity factor) for the onset of unstable crack extension in air. For the purposes of this study, the value of the stress intensity factor for the onset of unstable crack growth in these WOL specimens is referred to as K_{Iu}.

Two specimens of each material were loaded to a predetermined displacement by means of tightening a bolt to wedge open the precrack. The displacement was measured with a clip-gauge on the front face of the specimen, which was removed after torquing the bolt to the desired displacement. The applied K could be determined from the displacement measurement and the precrack location (determined from specimen compliance). The displacement was chosen to ensure that the precrack did not extend during initial loading. In addition, an instrumented reaction pin was used under the bolt, such that the load could be assessed and monitored with time. More details of the methodology to monitor load can be found in Nibur et al [4].

After loading to the desired displacement, all six specimens were placed into a pressure vessel with a feedthrough that enables monitoring the individual load signals from the instrumented reaction pins. The vessel was purged three times with high-purity helium, followed by purging three times with hydrogen. All purging was conducted between about 20 MPa and rough vacuum. Subsequently, the vessel was pressurized to 100 MPa with hydrogen. The quality of the gas in the pressure vessel was evaluated by taking gas samples both at the beginning and conclusion of the hydrogen exposure. These gas samples were evaluated by a commercial laboratory and found to contain about 4 ppm water. The total exposure time was slightly greater then 1000 hours.

At the conclusion of the hydrogen exposure, the specimens were removed from the hydrogen environment. The bolts were removed to unload the specimens. Then the specimens were fatigue cycled to mark the location of the crack as well as break open the specimens. The location of the precrack and subsequent crack extension could then be measured optically on the fracture surface.

Relationships for determining K

The K solution for the WOL specimen was reviewed by Nibur et al. [4]. They propose modifications to the relationship in the ASTM standard to account for the side grooves, which is different than the effective thickness relationship from the standard. The modified relationship essentially multiplies the standard equation by a correction factor, which we call $\bar{B}$. Therefore, the stress intensity factor (K_I) for a fixed displacement has the form

$$K_I = \bar{B}\frac{V_m E}{W^{1/2}} f(a/W) \tag{1}$$

where V_m is the crack-mouth opening measured on the front face of the specimen, E is the Young's modulus (68.9 GPa), a is the location of the crack,

$$f(a/W) = \left[(1-a/W)^{1/2}\right][0.654 - 1.88(a/W) + 2.66(a/W)^2 - 1.233(a/W)^3] \tag{2}$$

and

$$\bar{B} = \frac{(B/B_N)^{1/2}}{[2.48 - 2.89(B_N/B) + 1.41(B_N/B)^2]} \tag{3}$$

The value of $\bar{B}$ for the nominal dimensions from this study is 1.042, meaning that the value of K is nominally 4.2% greater than predicted by the standard relationships.

Additionally, to determine the onset of unstable crack growth for the modified bolt-load specimen under monotonic loading, the K solution was fit to the standard (type I) form for compact tension which has the form

$$K_I = \frac{P}{(WBB_N)^{1/2}} g(a/W) \tag{4}$$

where

$$g(a/W) = \left[\frac{(2+a/W)}{(1-a/W)^{3/2}}\right][32.834 - 246.35(a/W) + 778.44(a/W)^2 - 1233.7(a/W)^3 + 976.19(a/W)^4 - 307.7(a/W)^5] \tag{5}$$

Equation (4) and (5) are then used with the maximum load (P_u) to determine the stress intensity factor at the onset of unstable crack growth (K_{Iu}).

RESULTS AND DISCUSSION

In this study, the environmentally-assisted cracking (EAC) was evaluated by loading WOL specimens in air to a fixed displacement then immersing the loaded specimens in the environment of interest: high-pressure gaseous hydrogen. The maximum loading condition that could be achieved in these specimens is determined by the onset of unstable crack growth in air (since the specimens are loaded in air prior to immersion in the high-pressure hydrogen). Additionally, ISO 7866 requires evaluating sustained load cracking of aluminum alloys for pressure applications at an applied stress intensity factor (K_{IAPP}) of

$$K_{IAPP} = 0.056 \times S_y \tag{6}$$

where S_y is the 0.2% offset yield strength. Thus, sustained load cracking should be evaluated at stress intensity factors greater than K_{IAPP} and necessarily less than the onset of unstable crack growth K_{Iu}. Table 3 gives K_{IAPP} for the alloys in this study as well as the measured values of K_{Iu}. In the case of 7050, K_{IAPP} is greater than K_{Iu}, thus specimens cannot be loaded to accommodate the requirements of ISO 7866. Therefore, specimens of 7050 were loaded to fixed displacements that corresponded to about 80% of K_{Iu}. For the other two alloys, specimens could be loaded to a stress intensity factor greater than the values determined from the ISO standard. Thus, specimens were loaded to fixed displacements corresponding to stress intensity factors about 10% greater than K_{IAPP}.

Since the specimens were instrumented, the load was monitored after immersion in gaseous hydrogen at pressure of 100 MPa. If cracks had extended in the hydrogen environment, the load would have decreased since the displacement was fixed. However, in all cases, there was no definitive evidence of crack extension. Lack of crack extension during the hydrogen exposure was confirmed from observation of the fracture surfaces after breaking open the specimens. Therefore, the stress intensity factor associated with the loading condition was identified as K_{IEAC} as shown in Table 3.

These results suggest that these alloys in the given tempers are not susceptible to stress corrosion cracking in fuel cell grade high-pressure hydrogen. In contrast, Speidel showed that 7000-series aluminum alloys in T6X tempers are susceptible to sustained load cracking in 'wet' hydrogen [1]. However, those previous studies considered (i) higher-strength tempers where stress corrosion cracking is observed and (ii) water content that was generally higher than in this study. In this study, the 7000-series alloys were in the overaged condition (T7X temper), which is designed to minimize stress corrosion cracking. The 2219 alloy is significantly lower strength than the overaged 7000-series alloys, implying lower sensitivity to stress corrosion cracking. Fuel cell grade hydrogen allows up to 5 ppm water impurity and in this study the water content was measured to be 4 ppm, near the maximum allowable, but still relatively low.

Fatigue and fracture studies in high-pressure hydrogen have shown no evidence of hydrogen effects in aluminum alloys, which is likely due to the low solubility of hydrogen in aluminum alloys and the unfavorable thermodynamics of hydrogen dissociation on aluminum surfaces. Trace amounts of water do not seem to change energetics of hydrogen on aluminum surfaces. While these alloys could be susceptible to higher humidity air environments, there is no evidence that these alloys are susceptible to high-pressure hydrogen with up to 4-5 ppm water.

SUMMARY

Several aluminum alloys were evaluated for sustained load cracking in high-pressure gaseous hydrogen environments. Aluminum alloys 7050 and 7475 in T7X tempers and 2219 in the T851 temper show no evidence of hydrogen-assisted fracture or stress corrosion cracking in high-pressure gaseous hydrogen due with up to 4-5 ppm water. These results suggest that high-strength aluminum alloys can perform well in fuel cell applications, which permits hydrogen containing up to 5 ppm water.

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Table 1. Composition (wt%) of aluminum alloys evaluated in this study.

Alloy & temper	Zn	Mg	Cu	Ni	Si	Fe	Mn	Cr	Ti	V	Zr
7050-T7451	6.13	2.12	2.10	n/r	0.05	0.09	0.01	0.02	0.05	0.01	0.08
7475-T7351	5.90	2.12	1.47	n/r	0.05	0.06	0.01	0.20	0.04	0.01	0.00
2219-T851	0.05	0.008	6.49	0.004	0.04	0.11	0.30	0.000	0.03	0.07	0.12

Table 2. Tensile properties (from mill certification) for aluminum alloys in this study.

Alloy & temper	Yield strength (MPa)	Ultimate strength (MPa)	Elongation (%)
7050-T7451	450	517	7.0
7475-T7351	404	488	9.8
2219-T851	347	455	7.7

Table 3. Mechanical properties of the investigated aluminum alloys

Material	K_{IAPP} (MPa $m^{1/2}$)	K_{Iu} (MPa $m^{1/2}$)	V_m (mm)	K_{IEAC} (MPa $m^{1/2}$)
7050-T7451	25.3	24.9	0.475	19.8
			0.482	20.1
7475-T7351	22.7	36.9	0.648	27.2
			0.611	25.0
2219-T851	19.5	25.6	0.518	21.4
			0.517	21.2

