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Technical Reference on Hydrogen Compatibility of Materials

Aluminum Alloys, Non-Heat Treatable Alloys: Pure Aluminum (code 3001)

Prepared by:
C. San Marchi, Sandia National Laboratories

Editors
C. San Marchi
B.P. Somerday
Sandia National Laboratories

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Sandia National Laboratories
Matls Tech Ref
C. San Marchi (MS-9402)
7011 East Ave
Livermore CA 94550.

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1. General

The effects of hydrogen on aluminum alloys are not well understood; indeed, there is much conflicting information. Despite the perception that aluminum alloys are immune to gaseous hydrogen [1, 2], the micromechanics of deformation in aluminum are strongly affected by hydrogen [3, 4]. Aluminum alloys can be highly susceptible to stress corrosion cracking, which is generally interpreted to be due to hydrogen. The literature on this topic is extensive, although these tests are generally performed in aqueous or "wet" environments where the solubility of hydrogen is many orders of magnitude greater than hydrogen solubility from dry hydrogen gas. Based on the available experimental data obtained in hydrogen gas [5-7], aluminum alloys appear to have good resistance to hydrogen-assisted fracture in dry environments.

Thermodynamically, aluminum has a low solubility for hydrogen when in equilibrium with dry hydrogen gas [8]. Moreover, the native oxide acts as a kinetic barrier to hydrogen uptake since the kinetics of formation of atomic hydrogen (a necessary step to hydrogen uptake and hydrogen-assisted fracture) is limited on the oxide surface. In the presence of electrochemical environments and wet hydrogen, however, atomic hydrogen can be readily produced and enter the aluminum lattice [1]. Under these conditions, the solubility of hydrogen in aluminum can be very high, equivalent to many millions of atmospheres of dry hydrogen gas [9, 10]. Significant degradation of properties of high-strength aluminum alloys has been reported in "wet" hydrogen gas [1].

Hydrogen-assisted fracture in all materials depends on the characteristics of hydrogen transport; therefore, interpretation of testing results for aluminum alloys in hydrogen gas must be made with consideration of potential kinetic limitations on hydrogen transport. However, there are large variations in the literature data on hydrogen solubility and diffusivity [8, 11]. Studies of hydrogen transport in aluminum are complicated by the low solubility of hydrogen [8], the kinetic effects of the native oxide and the interactions of hydrogen atoms with vacancies [11, 12], as well as hydrogen trapping in some systems [8, 11].

2. Permeability, Diffusivity and Solubility

The solubility and diffusivity of hydrogen in aluminum are reviewed in Refs. [8, 11], showing significant scatter in the data. Reported hydrogen solubility values vary by six orders of magnitude when extrapolated to room temperature [8], with the largest reported value at room temperature being about 2.5×10^{-6} mol H_2 m^{-3} $MPa^{-1/2}$. The low solubility of hydrogen in aluminum makes it particularly difficult to quantify by gas extraction techniques, which does not distinguish between hydrogen dissolved in the metal and hydrogen trapped by specific metallurgical features [8]. Thus, care should be extended to the extrapolation of hydrogen solubility trends from high-temperature to ambient temperature [11]. Gas permeation experiments allow for determination of the rate of hydrogen transport through a metal at steady state (i.e., permeation), as well as the diffusivity of hydrogen through the metal by analysis of transport transients. Solubility is the ratio of permeability and diffusivity (Ref. [13] provides some background on the thermodynamic origin of the relationships between permeation, diffusion and equilibrium dissolution), thus hydrogen solubility can be determined accordingly.

Reported values of hydrogen diffusivity vary by at least two orders of magnitude at elevated temperature, and by many orders of magnitude at ambient temperature. In particular, diffusivity values extrapolated to ambient temperature from elevated temperature data appear to predict values at the low end of this spectrum. Several studies near ambient temperature, however, report consistent values for hydrogen diffusivity of about 10^{-11} m^2/s [8, 11, 12], significantly higher than extrapolated values. The discontinuity between hydrogen diffusivity in aluminum at high and low temperature is interpreted to be due to hydrogen trapping, especially the trapping by vacancies at elevated temperature [11, 12]. At low temperature, the vacancy concentration is sufficiently low that hydrogen transport is not limited by interactions with vacancies.

Aluminum is often considered to be a barrier to hydrogen permeation. The native oxide on aluminum metal is an effective kinetic barrier to hydrogen permeation, thus as long as the oxide maintains its integrity the effective permeation of hydrogen through aluminum appears to be kinetically limited by surface processes. Using the apparent upper bounds for solubility and diffusivity that are quoted above, the hydrogen permeability through the aluminum lattice at ambient temperature is about 2.5 x 10^{-17} mol H_2 m^{-1} s^{-1} $MPa^{-1/2}$. This value is many orders of magnitude greater than values extrapolated from elevated temperature and several orders of magnitude lower than estimates for stainless steels. The effective permeability of aluminum with native oxide, however, will be much lower since the kinetics of formation of atomic hydrogen on the oxide is very low.

3. Mechanical Properties: Effects of Gaseous Hydrogen

3.1 Tensile properties

3.1.1 Smooth tensile properties

The tensile properties of commercially pure aluminum are unaffected by testing in high-pressure gaseous hydrogen, Table 3.1.1.1. High-purity aluminum (99.993% annealed bar, S_u = 103 MPa) was also found to be unaffected by hydrogen pressure up to 52 MPa [5]. Similarly, 7039-T61 plate (S_u = 434 MPa) was unaffected by 69 MPa gaseous hydrogen [5].

3.1.2. Notched tensile properties

Notched tensile properties of commercially pure aluminum are not degraded by testing in high-pressure gaseous hydrogen, Table 3.1.2.1.

3.2 Fracture mechanics

No known published data in hydrogen gas for pure aluminum. Fracture mechanics data on high-strength aluminum alloys tested in hydrogen gas can be found in Refs. [1, 14]. The literature on the effects of hydrogen from environments (stress-corrosion cracking) is extensive and beyond the scope of this review; however, these effects can be substantial.

4. Metallurgical Considerations

Hydrogen trapping appears to play an important role in the hydrogen transport of aluminum and its alloys [8, 11], if not the micromechanisms of hydrogen-assisted fracture. Therefore,

interpretation of test results needs to be considered in the context of the specifics of the microstructural condition of the tested alloy.

5. References

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Table 3.1.1.1. Smooth tensile properties of nominally pure aluminum tested at room temperature in high-pressure helium and hydrogen gas.

Material	Thermal precharging	Test environment	Strain rate (s^{-1})	S_y (MPa)	S_u (MPa)	El_u (%)	El_t (%)	RA (%)	Ref.
O temper	None	34.5 MPa He	$x10^{-3}$	—	110	—	42	93	[6, 7]
	None	34.5 MPa H_2		—	110	—	39	93	

Table 3.1.2.1. Notched tensile properties of nominally pure aluminum tested at room temperature in high-pressure helium and hydrogen gas.

Material	Specimen	Thermal precharging	Test environment	Displace-ment rate (mm/s)	S_y (MPa)	σ_s (MPa)	RA (%)	Ref.
O temper	(1)	34.5 MPa He	69 MPa He	0.4 x 10^{-3}	—	124	20	[6, 7]
		34.5 MPa H_2	69 MPa H_2		—	172	21	

† yield strength of smooth tensile bar

(1) V-notched specimen: 60° included angle; minimum diameter = 3.81 mm (0.15 inch); maximum diameter = 7.77 mm (0.306 inch); notch root radius = 0.024 mm (0.00095 inch). Stress concentration factor (K_t) = 8.4.