Technical Reference on Hydrogen Compatibility of Materials

Aluminum Alloys, Non-Heat Treatable Alloys: Pure Aluminum (code 3101)

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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 susceptible to stress corrosion cracking [5], particularly high-strength alloys for which hydrogen-assisted fracture is one mechanistic interpretation of property degradation [1, 6]. The literature on stress corrosion cracking of aluminum alloys is extensive, although testing is generally performed in aqueous or "wet" environments where hydrogen concentrations that develop in aluminum are many orders of magnitude greater than hydrogen concentrations that develop from dry hydrogen gas. Based on the available experimental data obtained during relatively short-term exposure to hydrogen gas [7-9], aluminum alloys appear to have good resistance to hydrogen-assisted fracture in dry environments.

Thermodynamically, aluminum has a low equilibrium solubility for hydrogen [10]. 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 concentration of hydrogen in aluminum can be very high, equivalent to concentrations developed from many millions of atmospheres of dry hydrogen gas [11, 12]. Significant degradation of fracture properties of high-strength aluminum alloys has been reported in "wet" gases [1].

Hydrogen-assisted fracture in all materials depends on the characteristics of hydrogen transport [13, 14]; 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 [10, 15]. Studies of hydrogen transport in aluminum are complicated by the low solubility of hydrogen [10], the kinetic effects associated with the native oxide and hydrogen trapping, such as the interactions of hydrogen atoms with vacancies [15, 16] or other microstructural features [10, 15].

1.1 Composition

The Aluminum Association (AA) designations have been widely adopted for aluminum alloys. The nominally pure aluminum alloys are designated 1XX for cast alloys and 1XXX for wrought alloys. Common designations of commercially pure wrought aluminum include 1060 (99.6%) and 1100 (99%), while 1199 (99.99%) is a common super purity grade.

1.2 Other Designations

UNS A91060 (1060), UNS A91100 (1100), UNS A91199 (1199), UNS A91350 (1350)

2. Permeability, Diffusivity and Solubility

The solubility and diffusivity of hydrogen in aluminum alloys are reviewed in Refs. [10, 15], showing significant scatter in the data. Reported values for hydrogen solubility in pure aluminum vary by six orders of magnitude when extrapolated to room temperature [10], with the largest

reported value at room temperature being about 2.5 x 10^{-6} mol H_2 m^{-3} $MPa^{-1/2}$. The low solubility of hydrogen in aluminum makes it particularly difficult to quantify lattice hydrogen concentrations (and thus infer solubility) by gas extraction techniques, which do not distinguish between hydrogen dissolved in the metal and hydrogen trapped by specific metallurgical features [10]. Thus, care should be extended to the extrapolation of hydrogen solubility trends from high-temperature to ambient temperature [15]. 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. [17] 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 for pure aluminum 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 [10, 15, 16], significantly higher than extrapolated values. The discontinuity between hydrogen diffusivity extrapolated from high temperature and hydrogen diffusivity measured directly at low temperature is interpreted to be due to hydrogen trapping, especially the trapping by vacancies at elevated temperature [15, 16]. At low temperature, the equilibrium vacancy concentration is sufficiently low that hydrogen transport should not be limited by interactions with vacancies (unless the material is supersaturated with vacancies, i.e. contains high concentration of non-equilibrium vacancies due to the characteristics of materials processing).

Aluminum is often considered to be a barrier to hydrogen permeation. Indeed, 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 would be 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 (99.0%; alloy 1100) are unaffected by testing in high-pressure gaseous hydrogen, Table 3.1.1.1. Similarly, the tensile properties of high-purity aluminum (99.993% annealed bar, S_u = 103 MPa) were found to be unaffected by hydrogen pressure up to 52 MPa [7].

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, 18]. The literature on the effects of hydrogen from environments (stress-corrosion cracking) is extensive and beyond the scope of this review; however, these effects have been shown to be substantial for highly alloyed aluminum.

4. Metallurgical Considerations

Hydrogen trapping appears to play an important role on the hydrogen transport in aluminum and its alloys [10, 15], if not the micromechanisms of hydrogen-assisted fracture. Therefore, test results need to be interpreted in the context of the specifics of the microstructural condition of the tested alloy. In the case of pure aluminum, the vacancy concentration is a critical concern for hydrogen transport, particularly since aluminum can have artificially high concentrations of vacancies due to quenching processes.

Relatively large hydrogen contents in aluminum alloys can result from casting processes due to the high solubility of hydrogen in liquid aluminum [19]. There is a significant body of literature that addresses this issue for castings [20], which is beyond the scope of applications for high-pressure hydrogen gas infrastructure.

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.
1100 O temper	None	34.5 MPa He	0.67 x10^{-3}	—	110	—	42	93	[8, 9]
	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.
1100 O temper	(1)	34.5 MPa He	69 MPa He	0.4 x 10^{-3}	—	124	20	[8, 9]
		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.