**PROJECT 57: ALUMINUM FOR $H_2$ SERVICE**

Adam Freund (Mines)
Faculty: Suveen Mathaudhu (Mines) and Kester Clarke (Mines) and Amy Clarke (Mines)
Industrial Mentor: Atish Ray, John Carsley, Shawn Yu

This project initiated in Fall 2021 and is supported by, CANFSA with primary industrial guidance from Novelis Inc. The research performed during this project will serve as the basis for a Ph.D. thesis program for Adam Freund.

## 57.1 Project Overview and Industrial Relevance

In recent years, the need for the reduction of greenhouse gas emissions has increased significantly. In 2019, approximately 6.5 billion metric tons of $CO_2$ were released by the United States alone. 54% of these emissions came as byproducts of transportation and electricity production [57.1]. To curb this $CO_2$ production, interest in hydrogen as an energy source has been renewed. This is due to its high energy density (120 MJ/kg compared to gasoline's 44 MJ/kg) and its combustion cycle $2H_2 + O_2 = 2H_2O$, which lacks $CO_2$ formation [57.2]. Hydrogen can be incredibly problematic, however, as it causes embrittlement of metals under certain operating conditions. This has been seen in ferritic steels for approximately 140 years. Aluminum has been shown to resist hydrogen embrittlement much more effectively than steel due to its passivating oxide layer, but this layer can be disturbed and broken by mechanical deformation. This enables hydrogen embrittlement to occur, which significantly reduces part lifetime. This project will focus on understanding fundamental hydrogen embrittlement pathways in cast and wrought aluminum alloy samples as well as the effects of severe plastic deformation on hydrogen infiltration and embrittlement.

## 57.2 Previous Work

The study of hydrogen embrittlement of steel has been exhaustive, but the same cannot be said for the hydrogen embrittlement of aluminum. However, a new focus on aluminum has yielded strides in the field. It is well known that when water encounters unoxidized aluminum, the following reactions can occur:

$$2Al + 6H_2O = 2Al(OH)_3 + 3H_2$$
$$2Al + 3H_2O = Al_2O_3 + 3H_2$$
$$2Al + 4H_2O = 2AlO(OH) + 3H_2$$

These reactions are all highly exothermic and, regardless of the resulting aluminum compound, molecular hydrogen is produced and can then catalyze to become atomic hydrogen [57.3]. The hydrogen then binds through different trapping sites, defined as attractive, physical, and mixed traps. Attractive traps function in four ways, through stress and electrical fields, as well as chemical potential and temperature gradients [57.4]. Physical traps consist of high angle grain boundaries, voids, and particle-matrix interfaces. Most often the traps are mixed in nature, appearing as dislocations (where lattice distortion combines with stress field induced force). Hydrogen tends to creep further into a material as the energetics of traps discourage hydrogen leaving a material. This ultimately leads to multiple pathways of embrittlement: hydrogen enhanced decohesion (HEDE), hydrogen enhanced local plasticity (HELP), Hydrogen-mediated microvoid distribution, and hydrogen-induced cracking [57.5-9]. These mechanisms result in inter- and intragranular cracking, either through lowered cohesive energy or increased hydrogen concentration at grain boundaries and crack nucleation sites.

Studies show that, with prolonged exposure to hydrogen, the mechanical properties of aluminum suffer with reductions in ultimate tensile strength and ductility [57.8, 57.10]. The effects are most pronounced in underaged aluminum, which lacked $MgZn_2$ phases, relying entirely on Guinier-Preston zones for hydrogen sequestration [57.10]. Overaged aluminum, however, retains the greatest ductility. This trend extends to hydrogen susceptibility where overaged aluminum has the lowest concentration of hydrogen when compared to under and peak-aged samples [57.10-11]. This is, in part, due to the elimination of dislocations in the material, restricting hydrogen permeation [57.10]. Cyclic fatigue of aluminum exposed to hydrogen has also been explored to find more realistic modes of failure in parts. When subjected to saltwater conditions (3.5% NaCl solution), part lifetime was drastically reduced when compared to a sample in air [57.11]. Hydrogen embrittlement found within surface pitting, when coupled with cyclic fatigue, enhanced crack propagation by embrittling the crack tip [57.12].

DFT simulations and molecular dynamics have also been performed to examine the effect of hydrogen embrittlement through physical and chemical principles. It has been shown that the work required to sever Al-Al bonds drops as a hydrogen concentration increases [57.13]. The same can be said for the energy required for decohesion[57.13-14]. Ultimately, hydrogen lowers the energy needed for grain and bond displacement and this effect occurs regardless of cosegregant.

## 57.3 Recent Progress

### 57.3.1 Experimental Pathway Determination

To best test the differences in hydrogen susceptibility between wrought and cast aluminum, unaltered and plastically deformed samples will be tested through slow strain rate and cyclic fatigue testing in a pre-charged state to develop a baseline for mechanical properties. Microstructural properties will be explored through EBSD, EDS, XRD, and SEM. Samples will then be charged with hydrogen and subjected to the aforementioned mechanical testing methods to compare post embrittlement effects. Thermal desorption spectroscopy will be performed on charged samples to examine hydrogen concentrations in the respective materials, while EBSD will ascertain crack locations in relation to grain microstructure. EDS and XRD will help to locate hydrogen segregation and concentration. Future experiments will focus on severe plastic deformation via high pressure torsion to examine hydrogen pathways within aluminum with a high dislocation density.

### 57.3.2 Material Procurement

Aluminum 6xxx and 7xxx-series samples will be sourced to investigate the effects of hydrogen embrittlement on high strength two phase, precipitation strengthened alloys. This will allow for a more fundamental study of aluminum so as to prevent precipitate effects and hydrogen resistance pathways. Future examinations will utilize other aluminum alloys to elucidate hydrogen resistance with the presence of alloying elements and precipitates.

## 57.4 Plans for Next Reporting Period

For the next reporting period, the majority of work will focus on:

- Further Literature Review
- Start baseline experiments of wrought and cast aluminum
- Complete and optimize hydrogen charging setup
- Construct and optimize slow strain rate testing apparatus
- Construct and optimize cyclic fatigue testing apparatus

## 57.5 References

[57.1] "Sources of Greenhous Gas Emissions." EPA, Environmental Protection Agency, www.epa.gov/ghgemissions/sources-greenhouse-gas-emissions

[57.2] Thomas, George. "Overview of storage development DOE hydrogen program." Sandia National Laboratories 9 (2000).

[57.3] "Reaction of Aluminum with Water to Produce Hydrogen", DOE, Department of Energy, https://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/aluminum_water_hydrogen.pdf

[57.4] Pressouyre G. M. (1979). A classification of hydrogen traps in steel. A, 10(10), 1571-1573. doi:10.1007/bf02812023

[57.5] Louthan, M. R., & Dexter, A. H. (1975). Hydrogen embrittlement of 1100 aluminum. Metallurgical Transactions A, 6(8), 1655–1657. doi:10.1007/bf02641980

[57.6] Outlaw, R. A., Peterson, D. T., & Schmidt, F. A. (1981). Hydrogen partitioning in pure cast aluminum as determined by dynamic evolution rate measurements. Metallurgical Transactions A, 12(10), 1809–1816. doi:10.1007/bf02643763

[57.8] Shinko, T., Halm, D., Benoit, G., & Hénaff, G. (2021). Controlling factors and mechanisms of fatigue crack growth influenced by high pressure of gaseous hydrogen in a commercially pure iron. Theoretical and Applied Fracture Mechanics, 112, 102885. doi:10.1016/j.tafmec.2020.1028

[57.9] Dwivedi, S. K., & Vishwakarma, M. (2018). Hydrogen embrittlement in different materials: A review. International Journal of Hydrogen Energy. doi:10.1016/j.ijhydene.2018.09.201
[57.10] Qi, W. J., Song, R. G., Qi, X., Li, H., Wang, Z. X., Wang, C., & Jin, J. R. (2015). Hydrogen Embrittlement Susceptibility and Hydrogen-Induced Additive Stress of 7050 Aluminum Alloy Under Various Aging States. Journal of Materials Engineering and Performance, 24(9), 3343–3355. doi:10.1007/s11665-015-1616-9
[57.11] CHLISTOVSKY, R., HEFFERNAN, P., & DUQUESNAY, D. (2007). Corrosion-fatigue behaviour of 7075-T651 aluminum alloy subjected to periodic overloads. International Journal of Fatigue, 29(9-11), 1941–1949. doi:10.1016/j.ijfatigue.2007.01.0
[57.12] Chen, J., Zhang, X., Zou, L., Yu, Y., & Li, Q. (2016). Effect of precipitate state on the stress corrosion behavior of 7050 aluminum alloy. Materials Characterization, 114, 1–8. doi:10.1016/j.matchar.2016.01.022
[57.13] Wilson, B. T., Robson, J. D., & Race, C. P. (2020). Modelling Hydrogen Embrittlement using Density Functional Theory: A theoretical approach to understanding environmentally assisted cracking in 7xxx series aluminium alloys. MATEC Web of Conferences, 326, 04006.doi:10.1051/matecconf/202032604006
[57.14] Zamora, R. J., Baker, K. L., & Warner, D. H. (2015). Illuminating the chemo-mechanics of hydrogen enhanced fatigue crack growth in aluminum alloys. Acta Materialia, 100, 232–239. doi:10.1016/j.actamat.2015.08.031