Characterization, Positron Annihilation Spectroscopy, and Mechanical Testing of Hydrogen Embrittlement in Advanced High-Strength Steels

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This study determined the feasibility of positron annihilation lifetime spectroscopy (PALS) as a characterization technique of hydrogen embrittlement in advanced high-strength steels. ArcelorMittal M1700 martensitic steel 1.8 mm thick samples were hydrogen charged with an electrolytic cell and checked via temperature desorption analysis (TDA). Mechanical testing of uncharged and charged ASTM sub-size samples at various times after charging showed that charged samples had significantly lower percent elongation. Fracture surfaces of charged and uncharged Z-milled tensile specimens were characterized by microvoid coalescence. Charged annealed samples had smaller positron lifetimes by 13 and 3 picoseconds (ps) for τ_1 and τ_2 (short and long lifetime components) respectively, indicating that hydrogen was occupying vacancies. Charged Z-milled samples exhibited longer lifetimes by 9 and 7 ps for τ_1 and τ_2 respectively, suggesting that diffused hydrogen stabilized monovacancies. Results showed that PALS is a possible characterization technique for hydrogen embrittlement.

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Project Goal

The focus of this work is to compare hydrogen embrittlement susceptibility in annealed, Z-milled, and electrogalvanized martensitic steel samples by correlating mechanical testing, positron annihilation lifetime spectroscopy, temperature desorption analysis, and scanning electron microscopy.

Background

Advanced High-Strength Steels (AHSS) are classified as steels with a tensile strength greater than 500 MPa and complex microstructures with superior strength-ductility balance compared to conventional steels [1]. AHSS's are especially susceptible to the phenomenon of hydrogen embrittlement. This process is initiated by the dissociation of adsorbed hydrogen molecules on the metal surface followed by the diffusion of hydrogen atoms into the metal [2]. Once in solid solution with the metal, crack growth can lead to premature failure. Processing steps involving high temperatures and contact with hydrogen, such as hot-rolling and pickling, increase the steel's susceptibility to hydrogen embrittlement [3].

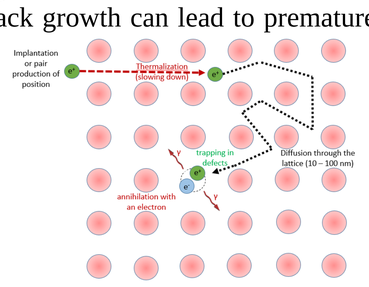

Figure 1 | Diagram of positron diffusion and annihilation in an atomic lattice.

A proposed method to characterize hydrogen embrittlement is positron annihilation lifetime spectroscopy (PALS). This technique utilizes the localization of positrons (positively charged particles with the mass of electrons) in sites of low electron density (vacancies, free volumes, voids, etc.) coinciding with locations where hydrogen molecules occupy [4]. When positrons collide with electrons, they annihilate, creating characteristic gamma rays that can be detected by a photomultiplier detector. The short lifetime component, τ_1, correlates to response in the bulk material whereas the long lifetime component, τ_2, correlates with the response in larger defects [4].

Material

The material of interest was an AHSS that is similar to ArcelorMittal's M1700 martensitic steel, see *Table 1* for M1700 composition. The effects of hydrogen embrittlement on this steel were analyzed after three processing steps: annealed, Z-milled (flatted with 2% plastic strain), and electrogalvanized (EG) with a 10 micron Zinc coating. Processing steps occur beginning with annealing and ending with EG coating.

Table 1 | Composition of ArcelorMittal M1700 martensitic steel [5].

	C	Mn	P	S	Other
M1700	0.30	0.45	0.01	0.015	B, Ti

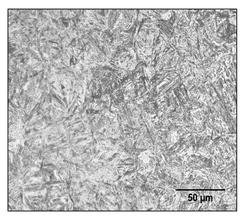

Figure 2 | Microstructure of annealed as-received sample.

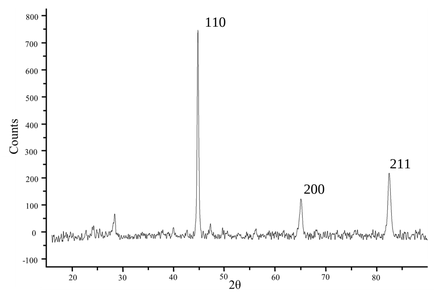

Figure 4 | XRD spectrum of Z-milled uncharged sample.

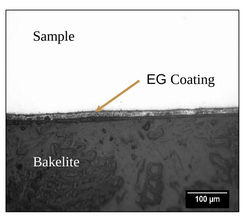

Figure 3 | Micrograph of EG coating.

XRD spectrum resembles a typical martensitic steel with peaks along the [110], [200], and [211] lattice directions at 2θ values of 45, 65, and 83 respectively.

Temperature Desorption Analysis

The Purdue and ArcelorMittal electrolytic charging cells gave similar results for diffusible hydrogen content via temperature desorption analysis (TDA). The first sample charged using the senior design team's cell showed additional trapped hydrogen, possibly due to local variability, although not conclusive. The hydrogen contents show little difference, meaning the charging cell was comparable to ArcelorMittal's cell.

Table 2 | Hydrogen amounts obtained by TDA of ArcelorMittal and Purdue samples.

	Purdue University		ArcelorMittal	
	Diffusible H content (≤250 °C), ppm	**Diffusible + Trapped H Content (≤900 °C), ppm**	**Diffusible H content (≤250 °C), ppm**	**Diffusible + Trapped H Content (≤900 °C), ppm**
1st Sample	1.61	4.42	1.61	1.96
2nd Sample	1.60	1.93	1.26	1.57
3rd Sample	1.44	1.70	1.79	2.08
Average	**1.55**	**1.82*** (exclude data from first sample)	**1.55**	**1.87**

Mechanical Testing

Uncharged annealed samples resulted in an average σ_{UTS} of 1760 ± 15 MPa with a total elongation of 7%. No significant difference in mechanical properties was shown between processing techniques, as shown by *Table 3*. Charged samples experienced less total elongation and showed more brittle fracture behavior in the stress-strain curve shown in *Figure 8*.

Table 3 | Average tensile strengths of Annealed, Z-Milled, and EG coated samples.

	Annealed	Z-Milled	EG Coated
Ave σ_{UTS} (MPa)	1760	1760	1751
Std Dev (MPa)	15	12	6

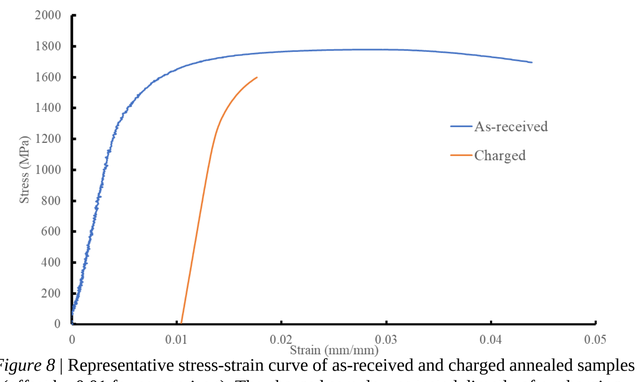

Figure 8 | Representative stress-strain curve of as-received and charged annealed samples (offset by 0.01 for comparison). The charged sample was tested directly after charging.

The study showed that percent elongation decreased significantly with hydrogen charging. *Table 4* shows that tensile tests performed at incremental time steps increased σ_{UTS} and percent elongation by 150 MPa and 2-5 % respectively over 7.5 hours for the annealed samples. As hydrogen diffused out of the sample, ductility at fracture partially recovered but did not return to the original ductile state in the as-received annealed sample.

Table 4 | Mechanical properties of annealed samples tested at given times after charging.

Condition	Time After Charging (hrs)	σ Yield (MPa)	σ Failure (MPa)	σ UTS (MPa)	Elongation (%)
Annealed	0	1520	1600	-	0.84
Annealed	1	1540	1660	-	1.02
Annealed	2	1540	1700	-	1.24
Annealed	4	1500	1680	-	1.13
Annealed	5	1530	1700	1730	1.48
Annealed	6	1530	1710	1740	1.51
Annealed	7.5	1510	1560	1750	4.87
Z-milled	0	-	1240	-	0.40
Z-milled	5	1540	1680	-	1.01
Z-milled	8	1540	1650	1680	2.42
EG	0	-	1430	-	0.53
EG	5	1550	1650	1710	3.43
EG	8	1550	1620	1730	4.22

Scanning Electron Microscopy

The fracture surfaces of Z-milled charged and uncharged samples were characterized by microvoid coalescence, which is characteristic of a ductile mode of fracture on the microscopic scale, as shown in *Figure 9*. Macroscopically the charged sample had significantly lower percent elongation.

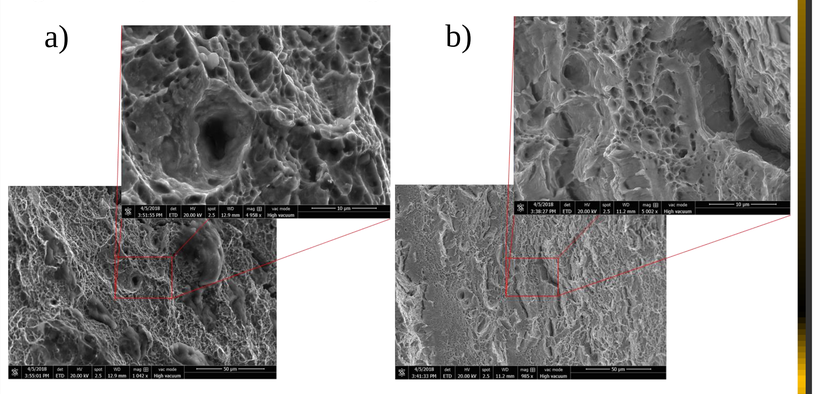

Figure 9 | Fracture surface SEM images of (a) hydrogen charged Z-milled tensile sample at nearly 1000x and 5000x magnification and (b) uncharged Z-milled tensile sample at nearly 1000x and 5000x magnification.

Positron Annihilation

The as-received annealed sample had a τ_1 of 159 picoseconds (ps) and τ_2 of 394 ps. Z-milled specimens increased τ_1 and τ_2 to 161 and 403 ps respectively. The change in τ_1 could be attributed to the prior plastic deformation, while the increase in τ_2 indicates the deformation promotes vacancy formation and coalescence. After charging, the short lifetime component of the annealed samples fell to 146 ps and the long lifetime component fell to 391 ps. This indicates hydrogen occupying vacancy locations and increasing the likelihood of the positron interaction, thus decreasing lifetime. Comparing the Z-milled charged and uncharged samples, an increase can be seen in τ_1 and τ_1 intensity, suggesting that hydrogen enhances monovacancy formation and subsequently stabilizes the vacancies [7]. This is supported by the decrease in τ_2 intensity.

Table 5 | PALS results of Annealed samples. As-received sample is after 24 hours and charged sample is after 6 hours.

Annealed As-Received	τ_1	τ_2
Lifetime (ps)	159	394
Lifetime Std Dev (ps)	3	6
Intensity (%)	56.7	42.5

Annealed Charged	τ_1	τ_2
Lifetime (ps)	146	391
Lifetime Std Dev (ps)	4	7
Intensity (%)	56.9	42.4

Table 6 | PALS results of Z-milled samples. As-received sample is after 24 hours and charged sample is after 6 hours.

Z-Milled As-Received	τ_1	τ_2
Lifetime (ps)	161	403
Lifetime Std Dev (ps)	3	6
Intensity (%)	57.3	42.0

Z-Milled Charged	τ_1	τ_2
Lifetime (ps)	170	410
Lifetime Std Dev (ps)	4	10
Intensity (%)	59.5	40.1

Conclusions

Time-based tensile testing along with comparing percent elongation showed that diffusible hydrogen remained in the samples up to six hours after charging, indicating that hydrogen is present throughout PALS testing. SEM showed failure by microvoid coalescence for charged and uncharged samples. TDA quantified the amount of hydrogen present. This research showed that PALS can characterize nanoscale defect size, however it is difficult to conclusively determine nanoscale mechanisms. The annealed samples' PALS results showed a decrease of τ_1 and τ_2 and were associated with the hydrogen occupying vacancy clusters. The Z-milled samples' PALS results showed an increase in τ_1 and τ_2, indicating that the additional strain produces hydrogen occupied monovacancies. Future work in the PALS field could include running shorter tests to account for hydrogen diffusing out of the specimen and further modification to allow low-temperature testing to prevent variability due to diffusing hydrogen.

Experimental Procedure

Hydrogen Charging

- Electrolytic Solution: 2.8% sulfuric acid in deionized H_2O by volume.
- Catalyst: Thiourea.
- Power Source: Current of 10 mA to two mossy titanium electrodes an steel sample held in place by Teflon slabs. Charged for one hour then stored in liquid nitrogen.

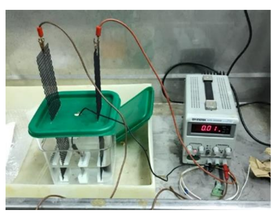

Figure 5 | Electrolytic cell constructed by the ArcelorMittal senior design team at Purdue with a power source.

Tensile Testing

Tensile testing was performed on an MTS tensile tester with a crosshead velocity of 5 mm/min. Samples were allotted resting times from 0 to 8 hours between charging and tensile testing to recover original ductility. A 25 mm MTS extensometer was used to measure strain.

Figure 6 | Fractured sample in the MTS tensile machine.

Positron Annihilation Spectroscopy

PALS was performed using a Na-22 source until 1 million counts were exceeded for uncharged samples. Hydrogen charged samples were tested for 6 hours, also using the Na-22 source. Data was analyzed using the PALSFIT program [6].

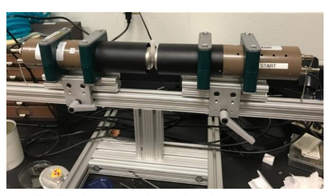

Figure 7 | Positron annihilation instrument used for the research at Purdue University.

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