

Hydrogen Embrittlement of Commercially Produced Advanced High Strength Sheet Steels

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ABSTRACT

The susceptibility of Advanced High Strength Steels (AHSS) to hydrogen embrittlement (HE) was evaluated on selected high strength sheet steels (DP 600, TRIP 780, TRIP 980, TWIP-Al, TWIP, and Martensitic M220) and the results were compared to data on a lower strength (300 MPa tensile strength) low carbon steel. Tensile samples were cathodically charged and then immediately tensile tested to failure to analyze the mechanical properties of the as-charged steel. The effects of hydrogen on deformation and fracture behavior were evaluated through analysis of tensile properties, necking geometry, and SEM images of fracture surfaces and metallographic samples of deformed tensile specimens. The two fully austenitic TWIP steels were resistant to hydrogen effects in the laboratory charged tensile samples. In contrast, with an increase in hydrogen content, all of the ferritic steels exhibited a decrease in tensile ductility and a transition in failure geometry from normal ductile fracture associated with localized through-thickness necking in flat tensile samples, to a more brittle fracture along a plane perpendicular to the maximum tensile stress. The dominant fracture surface feature observed for the steels susceptible to HE was a transition from ductile void coalescence when uncharged to transgranular cleavage in the charged condition; additionally, the fraction of the fracture surface that exhibited cleavage fracture increased with an increase in diffusible hydrogen content. Metallographic analysis showed the presence of internal voids and cracks that were primarily associated with second phase particles and increased in number with an increase in hydrogen content. Martensite, in particular untempered martensite in some deformed TRIP steel samples, appeared to be the constituent most susceptible to hydrogen content.

INTRODUCTION

Advanced High Strength Steels (AHSS) have been developed and applied in recent years with the goal to make lighter weight automobiles without sacrificing safety. AHSS steels in use today are primarily ferrite-based steels and include dual phase (DP), transformation induced plasticity (TRIP), complex-phase (CP), and martensitic (MART) steels. Selected austenitic steels, particularly twinning induced plasticity steels (TWIP), are also receiving considerable interest. The microstructures of ferrite-based steels are often complex and include controlled amounts of dispersed martensite islands, bainite, and retained austenite that transforms to martensite with deformation. Associated with the higher strengths and the presence of martensite in many of the structures is an increased concern for the potential of hydrogen embrittlement (HE), i.e. the degradation of mechanical properties (mainly ductility) in the presence of hydrogen. High residual stresses present due to transformation can contribute to the susceptibility by increasing the number of potential crack initiation sites [1,2,3], and as-quenched martensite has been shown to be the most susceptible phase to HE, due to the presence of high dislocation densities and residual stresses [1, 4, 5].

Hydrogen can be introduced during steel making, welding, or as a result of environmental interactions. During steel making and welding the presence of moisture in fluxes and slags offers a potential source of hydrogen which is dissolved in the liquid steel and retained on solidification. In solid steel products, hydrogen can be introduced in any environment that creates an electrochemical reaction. These include processing operations, e.g. acid cleaning and electroplating, or environmental interactions in service, e.g. interactions with moisture and highway salt during vehicle operation. Often steels that are prone to hydrogen embrittlement will undergo post-plating or post-forming heat treatments that enable the hydrogen to diffuse out, thereby greatly reducing potential for

Table 1. Chemical Composition and Thickness of As-Received Materials (in wt pct).

Material	C	Mn	P	S	Si	Cr	Al	V	Nb	Thickness (mm)
Low-C	0.035	0.19	0.011	0.014	-	-	0.045	-	-	1.0
DP600	0.08	1.69	0.028	0.02	0.028	0.029	0.1	0.04	0.01	1.07
TRIP780	0.19	1.59	0.013	0.002	1.63	0.03	0.036	-	-	1.2
TRIP980	0.24	1.69	0.008	0.001	2.13	<0.01	0.64	<0.01	<0.01	1.2
TWIP-Al	0.6	18	0.016	0.046	0.31	0.38	1.5	0.04	0.03	1.2
TWIP	0.6	18	0.018	0.095	0.048	0.01	0.03	0.09	0.02	1.2
M220	0.24	0.47	0.01	0.013	0.02	0.02	0.05	<0.008	-	1.2

embrittlement, since it is the diffusible not the residual hydrogen that causes embrittlement.

Several studies have evaluated the effects of hydrogen embrittlement in DP and other AHSS steels [2, 6, 7]. Davies [6, 7] examined hydrogen embrittlement effects on dual phase steels as a function of martensite volume fraction and observed that cracks and voids initiated at martensite/ferrite interfaces perpendicular to the tensile axis (TA). Hilditch *et al.* [2] observed similar characteristics in dual-phase and TRIP steels charged with hydrogen as well as a transition of fracture mode from ductile void coalescence to transgranular fracture which accompanied loss in ductility. Recent investigations in the use of twinning-induced plasticity (TWIP) steels, which utilize twinning as the dominant deformation mechanism as opposed to dislocation glide or phase transformation, have shown improved resistance to hydrogen delayed fracture [8, 9] with aluminum additions.

Although many studies have been performed on hydrogen embrittlement in high strength steels, limited data have been presented which correlate hydrogen levels with mechanical properties [2, 6, 7, 10]. Thus, the purpose of this study is to systematically evaluate the tensile properties of a series of AHSS steels with controlled variations in hydrogen content and correlate the observed sensitivity to hydrogen embrittlement to microstructural constituents present in each steel.

EXPERIMENTAL PROCEDURE

Four commercially produced high strength sheet steels (DP 600, TRIP 780, TRIP 980, and martensitic M220) were obtained along with two laboratory produced TWIP steels,

one with and one without an aluminum addition, and a lower strength (300 MPa tensile strength) low carbon steel used as a reference. The chemical compositions of the experimental steels are summarized in Table 1 which also includes a summary of the as-received sheet thicknesses. Full-thickness ASTM E8 longitudinal tensile samples were machined (end-milled) with a reduced gage section of 12.7 mm wide by 57.15 mm long.

<table 1 here>

The microstructures of the as-received materials were evaluated using standard metallographic techniques [11]. The dual phase microstructure consisted of ferrite and approximately 25% martensite; the TRIP steels consisted of retained austenite with bainite and/or martensite in a ferrite matrix; the TWIP steels are fully austenitic steels due to high alloying (18% Mn); the martensitic M220 steel consisted of a 100% tempered martensite microstructure; and finally the Low-C steel was ferrite with dispersed carbides. X-ray diffraction (XRD) analysis was performed on as-received as well as uncharged and deformed samples to determine retained austenite fractions. The TRIP steels contained different austenite contents pre-and post-deformation, indicative of an austenite to martensite transformation. The as-received retained austenite contents for the TRIP780 and TRIP980 were 14.8 and 1.6%, respectively. Post-deformation austenite contents were measured using XRD in the uniform elongation regions of tensile samples and were 2.5 and ~ 0% for the TRIP780 and TRIP980, respectively. It should be noted that the retained austenite content in the steel identified as TRIP980 was lower than anticipated; however, it will be referred to as a TRIP980.

Tensile samples and test coupons ($10 \times 7 \times$ sheet thickness (mm)) were cathodically charged with hydrogen using a DC power supply. Samples were immersed in a 1N H_2SO_4 electrolyte with an addition of As_2O_3 (1 or 10 mg/L) as a hydrogen recombination poison and a complete description of the charging system is presented elsewhere [11]. Hydrogen contents were measured with a LECO RH-404 hydrogen analyzer, and thus the results represent total hydrogen contents. Current densities ranged from 5 to 10 mA/cm^2 and charging duration ranged from 20 min to 6 hr, depending on the desired hydrogen level which, depending on steel, was as high as 26 ppm. Hydrogen content versus charging time curves were developed through triplicate tests and used to establish processing parameters for obtaining desired hydrogen levels [11]. The grips and fillets of the tensile samples were covered with a plastic coating to prevent charging. Immediately following charging, tensile samples were dried with a towel and tested in an electro-mechanical tensile test system. The time between charging and testing was approximately 90 s. Tensile tests were performed at an engineering strain rate of $3.3 \times 10^{-4} \text{ s}^{-1}$. A minimum of two tests was performed for each charging condition. Following tensile testing, internal damage was observed on polished metallographic cross sections and fracture surfaces were evaluated using a field emission scanning electron microscope (FE-SEM).

A set of tests were run to evaluate two additional variables on tensile testing and examine the sensitivity of hydrogen embrittlement to these variables. The first test examined strain rate effects on HE and the second examined the effects of a 24 hour room temperature age following the charge before tensile testing. The results of the tests can be found in [Appendix A](#).

RESULTS

MECHANICAL PROPERTIES OF AS-RECEIVED MATERIALS

[Figure 1](#) shows representative engineering stress strain curves for each experimental material in the as-received condition and [Table 2](#) summarizes measured average (minimum of two samples) yield strength, ultimate tensile strength and total elongations for each material. All materials satisfied the minimum properties for the specific material designation except for the TRIP980 which exhibited an ultimate tensile strength (948 MPa) that was slightly less than specified. [Figure 1](#) shows that the materials selected for this study exhibited significant differences in strength and ductility and offer a good representative group of AHSS materials for a study on hydrogen embrittlement.

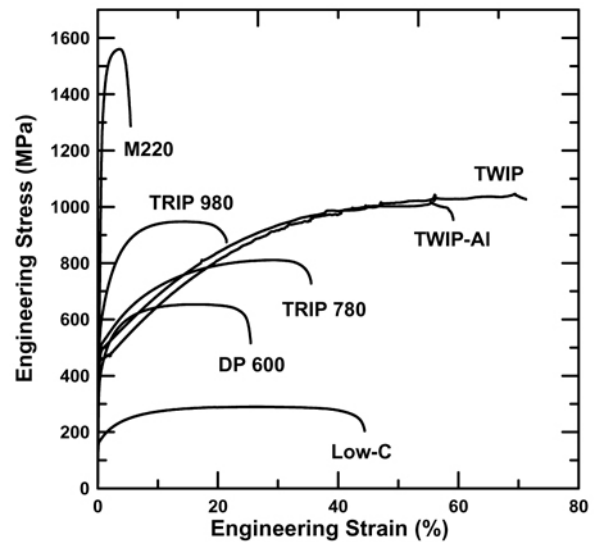


Figure 1. Engineering stress-strain curve of as-received Martensitic M220, TRIP980, TWIP, TWIP-AI, TRIP780, DP600, and Low-C mild steel tested at a constant strain rate of $3.3 \times 10^{-4} \text{ s}^{-1}$.

Table 2. Longitudinal Tensile Properties of As-Received Experimental Materials

Material	YS (MPa)	UTS (MPa)	Total EI (%)
DP600	390	654	25.4
TRIP780	500	811	35.5
TRIP980	574	948	21.9
TWIP-AI	471	1009	59.1
TWIP	458	1045	71.2
M220	1324	1560	5.5

EFFECT OF HYDROGEN ON MECHANICAL PROPERTIES

[Figure 2](#) shows the effects of hydrogen on the engineering stress strain curves for DP600 ([Fig. 2a](#)), TRIP780 ([Fig. 2b](#)), TRIP980 ([Fig. 2c](#)), martensitic M220 ([Fig. 2d](#)), and the low-C steel ([Fig. 2e](#)). Each figure includes the as-received stress-strain data from [Fig. 1](#) along with selected curves chosen to illustrate the effects of hydrogen, with the measured hydrogen contents indicated in the figures. All of the stress-strain curves shown in [Figs. 2a-e](#) include duplicate curves for equivalent hydrogen contents illustrating the excellent reproducibility that was observed in this study [11]. For example, in [Fig. 2b](#) duplicate samples are shown (indicated

by the numbers in parentheses) for each hydrogen content which when superimposed on the same plot exhibit nearly identical behavior. For each material, an increase in hydrogen resulted in a decrease in ductility without a significant change in the deformation behavior, i.e. the stress-strain data for hydrogen charged samples essentially superimpose on the data of the uncharged materials up to the strain where failure occurred. Furthermore, for each material, the post uniform strains in the hydrogen charged samples were essentially zero, as evident by the abrupt load decrease after peak load. The reproducibility and incremental loss in elongation were observed in the DP600, TRIP780, and TRIP980 in [Figs. 2a, 2b and 2c](#), respectively.

After hydrogen charging all samples exhibited measurable plastic deformation prior to failure except for the martensitic M220 steel, shown in [Fig. 2d](#), which exhibited failure in the elastic strain region prior to the onset of measurable plastic flow, even when charged with the smallest amount of hydrogen, 1.8 ppm. As discussed below, failure in the martensitic material was characterized as completely brittle.

The low-C steel, shown in [Fig. 2e](#), also exhibited a large loss in ductility with small amounts of hydrogen, however, the failure mode was distinctively different from the AHSS steels in this study. The observed ductility loss with hydrogen was interpreted to be due to blistering (i.e. surface roughening due to subsurface decohesion formation), shown in the surface photograph of a failed sample in [Fig. 3](#) in which only 0.9 ppm hydrogen was measured remaining in the sample. The presence of blistering, a consequence of hydrogen production and evolution from the sample, effectively decreased the load bearing area of the sample leading to premature ductile fracture as opposed to the brittle fracture mechanisms promoted by diffusible hydrogen and discussed below for the AHSS materials.

The two TWIP steels, not presented here, showed resistance to hydrogen effects in the cathodically charged samples [11]. The lack of susceptibility was attributed [11] to the consequence of low hydrogen diffusivity in austenite at room temperature, $D_{H^{\gamma}} \sim 10^{-12} \text{ cm}^2/\text{s}$ [12, 13] a value which is approximately 8 orders of magnitude lower than hydrogen diffusion in ferrite at room temperature. The low diffusivity limited the hydrogen introduced by the charging operation to the near surface regions, leaving the bulk material, and thus measured tensile properties, essentially unaffected. It should be noted that this observation differs from previous studies where TWIP steels without hydrogen charging were shown to be susceptible to delayed cracking where the hydrogen was interpreted to be present as a consequence of steel making operations and not introduced due to electrochemical interactions as considered here [8].

<figure 2 here>

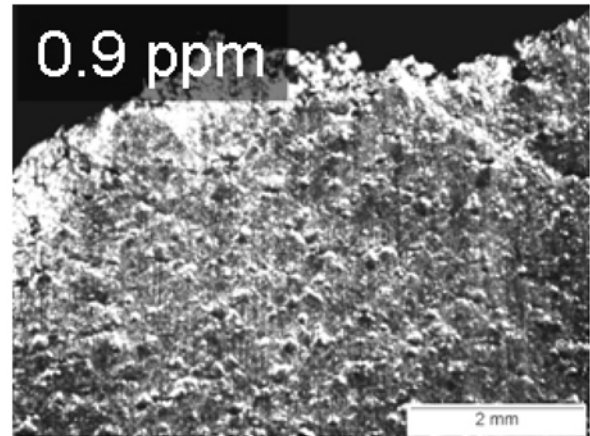


Figure 3. Photograph of surface blistering on Low-C steel tensile sample charged to 0.9 ppm H. Surface blistering was not observed on other steels examined in this study.

As shown in [Fig. 1](#), the strengths and ductilities of the experimental steels differed widely. To provide a method to compare the effects of hydrogen on loss in ductility, a normalized “total elongation loss,” shown in [Eq. \(1\)](#), was calculated for each sample and the results, as a function of hydrogen content, are plotted in [Fig. 4](#).

$$\text{Total El Loss}(\%) = \frac{(\%El_{\text{uncharged}} - \%El_{\text{charged}})}{\%El_{\text{uncharged}}} \times 100 \quad (1)$$

[Figure 4](#) shows the calculated total elongation loss percentages versus hydrogen content in ppm for each experimental steel. Consistent with observations discussed with [Fig. 2d](#), the martensitic M220 steel exhibited significant embrittlement at low hydrogen contents in which a few ppm of hydrogen results in over 90% loss in elongation and failure occurred before yielding. The TWIP steels exhibited essentially no effect of hydrogen due to the inability of the charging process to significantly alter the bulk hydrogen contents. The dual phase and TRIP steels exhibited systematic increases in ductility loss with an increase in hydrogen content.