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# The role of reversed austenite in hydrogen embrittlement fracture of S41500 martensitic stainless steel

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ABSTRACT

Up to now, the precise role of reversed austenite (RA) in hydrogen embrittlement (HE) of steel is still not fully understood. This work presents new observations and interpretation of fracture surface features immediately beneath the fracture surface for S41500 martensitic stainless steels (MSS) with aim to reveal the role of RA in HE resistance. The MSS were tensile tested with slow strain rate under electrochemical hydrogen charging condition. Steel containing more RA was found to have less hydrogen embrittlement susceptibility. Focused ion beam (FIB) was used to prepare sample for TEM observation of fracture path after HE fracture. It clearly shows that RA near the fracture surface has transformed to the newly formed martensite (NFM) and cracking occurs along both the tempered martensite/NFM boundaries and the lath boundaries. Three dimension atom probe (3DAP) confirms that RA is the H trapping site. Thus the beneficial role of RA is that it can act as a stable hydrogen trapping site which can increase the HE resistance by reducing hydrogen content at lath and grain boundaries. But its beneficial effect should not be overestimated since cracking along tempered martensite/NFM boundaries can occur after martensitic transformation as a result of hydrogen redistribution.

## 1. Introduction

Martensitic steels (MS) with multiphase microstructures are widely used in water turbines, automobile, and many other industry applications due to their high strength, high toughness, good weld property and so on [1–4]. Quenching and inter-critical tempered (Q&T) [5,6] or quenching and partitioning (Q&P) [7,8] heat treatments are usually used to obtain a mixture microstructure of soft austenite phase and hard martensite phase, which are beneficial to adjust the strength and toughness of steels. The formation mechanism of austenite [8–11] and the influence of austenite on the mechanical property of different steels [12–16] have been extensively investigated, and it is generally accepted that austenite formed with enrichment of austenite-stabilized element (Ni or C) can enhance the ductility and toughness of MS and martensitic stainless steels (MSS) through the transformation induced plasticity (TRIP) effect.

However, in practical applications, corrosion may occur and hydrogen can be generated by the cathodic reaction, which may cause HE and a premature failure [17,18]. There are three prevalent mechanisms with respect to HE, i.e., hydrogen-enhanced decohesion (HEDE) [19], hydrogen-enhanced localized plasticity (HELP) [20] and adsorption-induced dislocation emission (AIDE) [21]. HEDE mechanism (hydrogen causing a reduction in the cohesive bond strength) generally accounts for brittle cracking in the absence of significant local deformation. HELP mechanism (proposing hydrogen facilitating dislocation activity and promoting planar slip) usually accounts for localized plasticity and slip-band cracking [22]. AIDE mechanism (hydrogen adsorption accelerating dislocations emission at crack tip) normally accounts for nano-dimpled cleavage-like cracking, and has not received the same level of acceptance as HEDE and HELP [23]. Up to now, there is no unified theory to account for all the HE phenomena. A synergistic action of the above mechanisms may operate for HE fracture rather than a single one [24,25].

Lath martensite as a matrix phase in MS is a very susceptible microstructure to hydrogen embrittlement. Nagao et al. studied the hydrogen embrittlement of lath martensitic steel [24], and showed that a plasticity-mediated decohesion mechanism accounts for the

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hydrogen-induced features “flat” and “quasi-cleavage” created by failure along prior austenite grain and lath boundaries, respectively. Austenite as a plastic phase in martensitic steels has a lower diffusion rate (about $10^{-15}$–$10^{-16}$ $m^2/s$ for austenite, $10^{-10}$–$10^{-12}$ $m^2/s$ for martensite) and a higher solubility of hydrogen than the lath martensite [26–29] and can be an irreversible hydrogen trapping site with a relatively high binding energy of 55 kJ/mol [30–33]. Thus, austenite would have great influence on the HE resistance. Li et al. found that reversed austenite (RA) impeded the inward transportation of hydrogen to crack tip, and thus increased the HE resistance of PH 13-8 Mo martensitic stainless steel [34]. Yang et al. compared a Q&P steel with a Q&T steel [35], and found that Q&P steel with some refined retained austenite had a higher resistance to HE than Q&T steel. They explained that austenite can retard diffusion and increase the solubility of hydrogen. However, deleterious effect of retained austenite on HE resistance was also reported in literature. For example, Park et al. claimed that retained austenite is a “source” of hydrogen after deformation induced martensite transformation and can accelerate the HE failure of the welded martensitic steels [31]. Zhu et al. also found that the retained austenite can decrease the HE resistance of Q&P steel [30]. Austenite is a metastable phase in martensitic steels, and will transform to martensite under stress (or strain) and hydrogen attack [36] since hydrogen can decrease the stacking fault energy (SFE) of austenite [37,38]. Therefore the stability of austenite may also have a great effect on the HE fracture, which makes this issue more complicated. On this basis the precise role of austenite on the HE fracture of MS is still not fully explored. Most studies are based on macroscopic observations. Detail view of the fracture feature and observations of hydrogen distribution in nanoscale are still lacking, which are necessary in order to reveal the relationship between the microstructure and the fracture path.

Recently, the development of three-dimension atomic probe (3DAP) has provided a way to obtain a three-dimensional compositional imaging with a high resolution at the atomic scale, especially for hydrogen distribution, which can not be detected by traditional methods such as energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) et al. [39,40] Focused ion beam (FIB) technique has been successfully used to make sample normal to the fracture surface from site-specific location for a transmission electron microscopy (TEM) observation [24,41–43]. TEM observation of FIB sample can provide atomic view of the fracture feature underneath the fracture surface and evolution of dislocations during the HE fracture, which can help to understand the relationship between crack propagation direction and microstructure [24].

In this study, HE resistance of two kinds of MSS with identical composition but different heat treatment was compared through a slow strain rate test (SSRT) in the air and hydrogen environment. The fracture surface features were observed by scanning electron microscopy (SEM), and FIB samples were made for TEM investigations with aim to obtain more details of crack propagation feature and microstructure after fracture. Meanwhile, 3DAP was also used to reveal a spatial elemental distribution of the bulk alloy. Finally, the actual role of RA on HE resistance for a commercial S41500 MSS has been explored.

## 2. Experimental

### 2.1. Materials

A UNS S41500 low carbon MSS was used in the present study, and the chemical compositions are given in Table 1. The alloy was austenitized at 1050°Cfor 2 h and then water quenched. Double tempering (680 °C for 2 h, 630 °C for 2 h) and single tempering (630 °C for 2 h) treatments were conducted to make the final alloys, which are referred to as DT (double tempering) and ST (single Tempering) respectively. The heat treatment procedure is schematically illustrated in Fig. 1.

**Table 1**
Chemical compositions (mass%) of the investigated martensitic stainless steel.

| C | Cr | Ni | Mo | Mn | P | S | Fe |
|---|---|---|---|---|---|---|---|
| 0.042 | 13.09 | 4.08 | 0.57 | 0.73 | 0.021 | 0.0024 | Bal. |

### 2.2. Microstructural observations

Optical microscopy (OM), SEM (XL30-FEG-ESEM) with a back scattered electron (BSE) model and TEM (JEOL-2100F) attached with an energy dispersive X-ray spectroscopy (EDX) were used to investigate the microstructure of the samples. Specimens for OM observation were etched with Vilella's reagent (1 g picric acid + 5 mL HCl + 95 mL ethanol). Thin foil for TEM observation was jet polished with a solution of 10% perchloric acid ($HClO_4$) and 90% ethanol. For SEM/BSE and X-ray diffraction (XRD) analysis, the specimen surfaces were polished in alumina suspension (0.05 μm) to remove the mechanically damaged layers. XRD analysis was carried out using CuKα radiation at 50 keV. The volume fraction of RA for DT and ST alloys was evaluated using the following equations [44],

$$V_{\alpha'}+V_{\gamma}=1, \tag{1}$$

$$V_{\gamma}=\frac{1.4I_{\gamma}}{I_{\alpha'}+1.4I_{\gamma}}, \tag{2}$$

where $V_{\alpha'}$ and $V_\gamma$ are the volume fraction of martensite and RA, respectively. $I_{\alpha'}$ and $I_\gamma$ are the integrated intensities of $(1\ 1\ 0)_{\alpha'}$ and $(1\ 1\ 1)_{\gamma}$ peak, respectively.

### 2.3. Elemental distribution by 3DAP

The three-dimensional atom probe (3DAP) sample was mechanically cut from the bulk material with a size of 0.5 × 0.5 × 20 $mm^3$, and then a two-step electro-polishing was used to make the final sample at the room temperature. An electrolyte of 25% perchloric acid in acetic acid at a direct current of 15 V

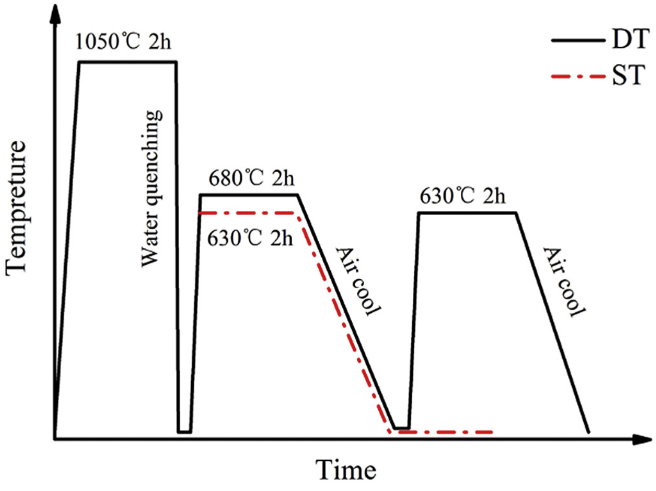

**Fig. 1.** Schematic illustration of the heat treatments.