# Effect of retained austenite on the hydrogen embrittlement of a medium carbon quenching and partitioning steel with refined microstructure

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**ABSTRACT**

The effect of retained austenite on the hydrogen embrittlement of a medium carbon quenching and partitioning steel was investigated by comparison to a traditional quenching and tempering steel with an identical chemical composition. Electrochemical precharging reduces the plasticity, including the elongation and reduction in area, of both steels, and the embrittlement phenomenon is more severe in the quenching and tempering steel based on a slow strain rate tensile test. As a result, the ultimate tensile strength decreases, as well. The fracture mode was dominated by intergranular features in the areas containing hydrogen, suggesting the weakening of boundary cohesion. Retained austenite, which retards diffusion and increases the solubility of hydrogen, is stable under the attack of hydrogen, contributing to the high hydrogen embrittlement resistance of quenching and partitioning steel. Refining the microstructure further improves plasticity due to the lower hydrogen content per area. In general, the quenching and partitioning steel with a refined microstructure exhibits the lowest hydrogen embrittlement susceptibility.

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## 1. Introduction

The application of advanced high-strength steels (AHSS) is favourable for the lowering of carbon emissions, weight reduction and satisfaction of safety requirements of cars in the automobile industry [1]. The development of steels consisting of martensite and austenite is one of the most promising innovations to achieve improved strength and plasticity simultaneously. This development was realized by Speer et al. [2] ten years ago using a novel heat treatment technique called quenching and partitioning (Q&P). After Q&P treatment, more than 5 vol% retained austenite exists in a martensitic matrix, contributing to excellent plasticity [3,4].

During the manufacture and service of steel components, hydrogen atoms are susceptible to permeate into the steel interior [5]. The potential processes that can lead to this include cathodic protection, phosphating, pickling, electroplating and arc welding. The hydrogen atoms in the steel then react with themselves or other chemical elements. As a result, hydrogen-induced corrosion, typically realized as hydrogen blistering, methane bubbles, hydrogen embrittlement (HE) and hydride formation, may occur and have a diverse range of harmful effects on steels [6]. However,

because of their different crystalline lattices, martensite and austenite act differently as the solvent and diffusion channel of hydrogen atoms in steel [7,8], and their mechanical properties are also different under the attack of hydrogen. In general, martensite exhibits a very high HE susceptibility [9,10]. Many studies have found that the solubility of hydrogen is very low but its diffusivity is very high in the martensitic lattice [11–14]. The segregation of hydrogen atoms on the boundaries, such as on the lath interface and grain boundary of the prior austenite, can weaken the boundary cohesion and thus promote cracking nucleation and growth along these boundaries [13,15]. Refining the martensitic microstructure has been demonstrated to be an effective method to improve the HE resistance in traditional quenching and tempering (Q&T) steels as a whole [16,17]. Conversely, austenite has a higher solubility for hydrogen and therefore, can sustain higher hydrogen contents without degradation [18]. However, part of austenite may transform to martensite when the hydrogen content exceeds a critical value, such as in certain metastable austenitic stainless steels [19,20]. In this case, the stability of austenite is highly important for good HE resistance.

There have been several recent investigations on HE in Q&P steels [21,22]. Lovicu et al. [21] compared a Q&P specimen to a Q&T specimen with identical chemical composition and similar ultimate tensile strength (UTS, $\sigma_b$). It was determined that the Q&P specimen with 17.5 vol% retained austenite has a higher HE

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susceptibility than the Q&T specimen with a negligible amount of retained austenite. They explained this phenomenon by arguing that austenite can trap more hydrogen atoms than the martensitic matrix during cathodic charging. The amount of these atoms hardly changes in the freshly formed martensite through deformation induced transformation of austenite, resulting in a high nucleation probability of micro-cracks. However, it is believed that the martensite in the Q&P specimen is harder than in the Q&T specimen because of its similar UTS level. Because the HE susceptibility of martensite shows a positive strength dependence, it is unclear which one, the harder martensite or retained austenite, acts as the HE promoter in this research. Zhu et al. [22] found that the hydrogen content in the retained austenite is three times greater than in martensite, as determined by three-dimensional atom probe tomography (3DAPT). Hydrogen-induced cracking may initiate at the martensite/austenite interface and then propagate through retained austenite and martensite. Similar to the Q&T specimen, the typical fracture mode is also intergranular. This study indicates that the existence of retained austenite decreases the HE resistance of Q&P steel, although the comparison to the Q&T specimen was not made in their paper.

Considering that the role of retained austenite in Q&P steel remains unclear and that its stability under the attack of hydrogen and its interaction with hydrogen, including diffusivity and solubility, may affect the mechanical properties and fracture mode of Q&P steel, the present work aims to investigate the relationship between retained austenite and the HE resistance of the Q&P steel. Because the refinement of the martensitic microstructure can be obtained only by adjusting the austenitization parameters, its effect was also compared with that of the retained austenite.

## 2. Material and experimental procedures

A medium carbon steel with a nominal composition Fe-0.4C-1.5Mn-1.5Si (wt%) was prepared by vacuum induction melting and casting. The critical temperature for austenitization ($Ac_3$) is 820 °C and starting temperature for martensitic transformation ($M_s$) is 307 °C, as determined by using J-MatPro software. The sheets annealed at 1000 °C were hot rolled from 10 mm to 1.5 mm by 9 passes continuously and then air cooled to room temperature. Subsequently, the rolled sheets were austenitized at 860 °C or 950 °C for 5 min, and then some of them were immersed in a molten salt bath at a temperature of 240 °C ($T_q$) for 15 s. After that, they were immediately transferred into another molten salt bath with a temperature of 420 °C ($T_p$) for 30 seconds and finally quenched in water. This processing prepares Q&P 860 and Q&P 950 specimens. The temperature $T_q$ was calculated based on CCE theory and the K-M equation, and $T_p$ was selected to avoid possible temper embrittlement [2,4]. For reference, other sheets were quenched into water directly from 860 °C or 950 °C after 5 min holding and then tempered at 420 °C for 120 s to prepare Q&T 860 and Q&T 950 specimens with nearly same UTS level with respect to Q&P partners, because HE susceptibility of steel shows positive dependence of UTS strongly. The longer tempering time may cause the precipitation of unexpected carbides. Since there is significant deviation on the volume fraction of martensite evaluated by using K-M equation, the dilatation curves of hot-rolled specimens were measured by DIL 805 A/D quenching and deformation dilatometer. The actual $M_s$ temperature of the specimen cooled from 860 °C or 950 °C was determined from inflection point, respectively, and corresponding volume fraction of martensite (initial martensite) quenched to $T_q$ was calculated from these curves.

The specimens for optical micrographs(OM) were prepared according to the normal procedure, that is, mechanical grinding with SiC grit papers and polishing with 0.5 μm diamond paste

followed by cleaning with soap solution, water and ethanol. Next, the samples were etched with a hot saturated picric acid solution containing sodium metabisulphite to reveal the grain boundary of the prior austenite. In addition, the refinement degree of the martensitic microstructure was examined by a JEOL 7600 F scanning electron microscope (SEM) operated at 15 kV. The solution for surface etching is 4% nital. The fractographic analysis after the tensile tests was also finished by SEM observation.

The OVA Nano 230 SEM, equipped with a field emission gun and a TSL system, was used to reveal the microstructure of the specimens, together with the electron backscatter diffraction (EBSD) analyses with step size of 20 nm. Orientation imaging microscopy (OIM) Analysis 5.2 software was used to interpret the EBSD results. EBSD micrographs were presented by combining the band contrast map and inverse pole figure map of the austenite grains.

Crystallographic features of retained austenite and martensite were further examined by transmission electron microscopy(TEM) observations by operating 2100 F TEM at 200 kV. The foils for TEM observation were prepared by twin-jet polishing using a solution 5% perchloric acid in ethanol at −20 °C.

The possible phases in both the Q&P and Q&T specimens were identified based on the X-ray diffraction(XRD) profiles obtained by Cu Kα radiation using a D/max-2550 X-ray diffractometer. The carbon concentration in the retained austenite in the Q&P specimens were obtained from the relationship between the lattice parameter $a_\gamma$ and the carbon concentration wt% C [23]:

$$a_\gamma(\text{Å}) = 3.573 + 0.033(\text{wt\% C}) \tag{1}$$

The volume fraction of retained austenite ($f_\gamma$) in the Q&P specimens was determined by means of magnetization measurement in a Quantum Design Physical Property Measurement System (PPMS-9T) by the method proposed by Zhao et al. [24]. The fully annealed specimen, which contains only ferrite plus pearlite, was used as the reference sample of austenite-free (AF).

Dog bone specimens with a gauge size 15 × 5 × 1.4 mm, along the longitudinal direction, were prepared by spark cutting and were grinded with water-proof paper to eliminate a possible notch effect. All areas besides the gauge area of each specimen were sealed with liquid paraffin before electrochemical precharging. The solution selected is 0.2 mol/L NaOH with 2 g/L thiourea as a promoter, and the precharging current density was 10 mA/cm².

The precharged specimens were subjected to slow strain-rate tensile (SSRT) tests using a Zwick/Roell Z020 with a constant strain rate of $5 \times 10^{-5}$ s⁻¹. Two tests were performed for each charging time to calculate the average mechanical properties in addition to confirming reproducibility. The yield stress (0.2% offset stress, $\sigma_{0.2}$), UTS ($\sigma_b$) and elongation after fracture ($\delta$%) were read directly from the engineering stress-strain curve. To evaluate the impact of the HE degree, an embrittlement index (EI) was defined as the fractional decrease in elongation ($\delta$%) or reduction in area ($\gamma$%), expressed as below

$$\delta_{loss}(\%) = \frac{(\delta_{air} - \delta_{charged})}{\delta_{air}} \times 100\%$$

$$\gamma_{loss}(\%) = \frac{(\gamma_{air} - \gamma_{charged})}{\gamma_{air}} \times 100\% \tag{2}$$

where the subscripts loss, air and charged denote plasticity loss and the specimens tested without and with precharging, respectively.

At same time, the relationship between the hydrogen content in the specimen and the precharging time was measured by the hot extraction method with a LECO TCH-600 hydrogen analyser. Specimens of size φ5 × 60 mm were prepared, and their surfaces