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Effect of ferrite on the hydrogen embrittlement in quenched-partitioned-tempered low carbon steel

Jilan Yang[a], Yisi Song[a], Yufei Lu[a], Jianfeng Gu[b], Zhenghong Guo[a,*]

[a] *Institute of Materials Modification and Modelling, School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China*
[b] *Collaborative Innovation Center for Advanced Ship and Deep-Sea Exploration, Shanghai Jiao Tong University, Shanghai 200240, China*

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ABSTRACT

This article proposes a novel method for the reduction of the hydrogen embrittlement susceptibility in a low carbon steel by the introduction of the ferrite phase into the quenched-partitioned-tempered (Q-P-T) specimen. Taking the Q-P-T specimen without ferrite as the reference, the CQ-P-T and QCQ-P-T specimens containing ferrite were obtained by intercritical annealing before the Q-P-T treatment and by pre-quenching before the CQ-P-T treatment to further refine the microstructure. The susceptibility of the three kinds of specimens toward hydrogen embrittlement was evaluated by the slow strain rate tensile test. The results showed that the elongation and area reduction of the three kinds of specimens continuously decrease with the greater electrochemical precharging time, but the three kinds of specimens exhibited different susceptibility index values. Fractographic observation showed that the primary fracture modes gradually evolved from typical dimple to quasi-cleavage, quasi-cleavage mixed with intergranular cracking and then complete intergranular manner, but the evolution rate of the QCQ-P-T specimen is the lowest while that of the Q-P-T specimen is the highest. It is suggested that the ferrite may reduce the stress concentration caused by the martensitic transformation and retard the crack propagation during deformation. Refining microstructure further improves the hydrogen embrittlement resistance by trapping more hydrogen atoms at the interphase boundary, lowering their density in the lattice.

1. Introduction

Once steel comes into contact with atomic or molecular hydrogen during various manufacturing operations or service, the hydrogen may be introduced into the matrix accidentally and then preferentially segregates on the grain boundary, dislocation or other traps [1–3]. When the hydrogen concentration reaches a threshold value, the steel becomes brittle, exhibiting the reduction of ductility, toughness and/or tensile strength until it cracks open (hydrogen induced cracking). Generally, the susceptibility to hydrogen-induced embrittlement shows a positive dependence on the steel strength. Especially when the ultimate strength exceeds 1000 MPa, the steel is very sensitive to the attack by hydrogen, so that an extremely low hydrogen concentration may cause delayed fracture without early warning [1–5]. Regarding the relationship between the strength and microstructure, different phases in steel have been shown to exhibit different hydrogen embrittlement susceptibilities because of their different strengths [2,4]. For example, the well-known conclusion has been reached that the hard martensite rather than the soft austenite in steel will undergo hydrogen embrittlement more easily [2,6]. By now, several mechanisms, mainly including high-pressure bubble formation, weakening of lattice bonding, reduction of surface energy, hydrogen-enhanced localized plasticity and hydride formation, have been proposed to interpret different brittle phenomena connecting to the related microstructure [1,3]. Therefore, elimination of the hydrogen embrittlement risk of high-strength steel by microstructural optimization is of the highest importance and can be realized based on the understanding of these mechanisms with a particular focus on the interaction between hydrogen and the different phases.

In recent years, there has been an increasing demand for the development of low-cost (usually Fe-Mn-Si-C series) advanced high strength steel (AHSS) by designing complex multiphase microstructure in order to achieve a balance of the high strength and good ductility. Among these, the novel quenched-partitioned-tempered (Q-P-T) steel, modified from the quenched and partitioned (Q&P) version by the addition of carbide formation elements such as Nb and V, has shown promising mechanical properties with the excellent combination of high strength and acceptable ductility [6–10]. In this kind of steel, the partial quenching results in the dual-phase microstructure composed of martensitic matrix and some untransformed austenite. The subsequent

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* Corresponding author.
E-mail address: zhenghongguo@sjtu.edu.cn (Z. Guo).

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isothermal holding by a "one-step" or "two-step" process allows the precipitation of alloying carbide such as vanadium carbide in the martensitic matrix simultaneously accompanying the carbon partitioning from martensite into austenite [7]. The formation of alloying carbide compensates for the drop of martensitic strength due to carbon depletion, while the enrichment of carbon in untransformed austenite improves its stability to avoid a further transformation upon subsequent rapid cooling to room temperature, which then contributes to the good ductility. As a result, elongation of more than 15% can still be obtained easily even though the ultimate strength is higher than 1000 MPa in the low or medium carbon Q-P-T steel [7–10].

Since the Q-P-T steel also belongs to the high-strength scale, its potential hydrogen embrittlement feature and method for possible improvement of resistance should be investigated for further applications. In this aspect, several researchers have paid much attention to the positive effect of the retained austenite and transitional ε carbide in martensite on the decrease of hydrogen embrittlement in the Q&P steels [6,11–13]. They noted that both austenite and transitional ε carbide are preferential hydrogen traps that weaken the attack of hydrogen on the martensitic matrix. In addition, the microstructural refinement was also found to provide additional hydrogen trapping to reduce the hydrogen concentration in martensitic lattice [6]. These results indicate that the Q-P-T steel may show a better resistance to hydrogen embrittlement than the Q&P steel because the alloying carbide (NbC or VC) has a stronger capability to capture the hydrogen atoms than the ε carbide. However, this does not mean that no further improvement by microstructural adjustment using different heat treatment parameters is possible. Based on the positive effect of ferrite on the hydrogen embrittlement in dual phase (DP) and transformation-induced plasticity (TRIP) steels, intercritical austenitization before the Q-P-T treatment may be a reasonable process for the introduction of some ferrite into steel for achieving a better hydrogen embrittlement resistance [2,4]. In this work, a low carbon steel was selected to study the effect of ferrite on hydrogen embrittlement resistance in the microstructural refined Q-P-T specimen.

2. Experimental procedure

The received low carbon plate was 1.5 mm thick after hot rolling. Its characteristic temperatures for heat treatment, A_{c1} (Austenite start temperature), A_{c3} (Austenite finish temperature), M_s (Martensite start temperature) and M_f (Martensite finish temperature) were measured by dilatometer tests and are listed in Table 1 together with their chemical compositions.

Three blocks were obtained from the plate by spark cutting. The first block (named Q-P-T) was annealed at 910 °C for 300 s and then quenched into molten salt at 300 °C for 15 s. It was then transferred to another molten salt at 420 °C for 30 s and quenched into water. The second block (named CQ-P-T) was intercritically annealed at 840 °C for 300 s, and then cooled with the same operation as the above-mentioned Q-P-T specimen. The third block (named QCQ-P-T) underwent the same heat treatment as that of the CQ-P-T specimen after pre-quenching from 910 °C. The purpose of the intercritical annealing is to introduce the desired ferrite into the steel while additional pre-quenching is carried out in order to further refine the microstructure of the specimen [14–16].

The sample for optical microscopy observation was prepared by etching first in a 4% nital solution and the fracture feature of the specimen after the tensile test was examined by a JEOL 7600F scanning electron microscope (SEM) operated at 15 kV, while the details of the carbide distribution and martensite and retained austenite morphologies were characterized by a JEOL 2100 F transmission electron microscope (TEM) observation operated at 200 kV. Prior to the TEM observation, the foils with the diameter of 3 mm were prepared by the twin-jet procedure in a 5 vol% perchloric acid in ethanol solution at −20 °C.

Table 1
Chemical composition (wt%) and characteristic temperature (°C) of the steel received.

Chemical composition (wt%)					Characteristic temperature (°C)			
C	Mn	Si	Cr	V	Ac_1	Ac_3	M_s	M_f
0.19	1.46	1.50	0.6	0.15	785 ± 5	890 ± 5	382 ± 5	173 ± 5

The volume fraction of the retained austenite (f^{γ}, vol%) and its carbon concentration (x^{γ}, wt%) were measured by a D/Max-2550 X-ray diffractometer (XRD) using Cu K_{α} radiation operated at 40 kV and 30 mA. The scanning angle (2θ, °) was varied from 30° to 120° at the scanning rate of 2°/min. f^{γ} was calculated by the direct comparison method from the integrated intensities of the $(200)_{\alpha}$, $(211)_{\alpha}$ (martensite, α) and $(200)_{\gamma}$, $(220)_{\gamma}$, $(311)_{\gamma}$ (austenite, γ) diffraction peaks [17,18], and the x^{γ} was simply estimated from the lattice parameter of the austenite (α_{γ}, Å) measured using Eq. (1) [19]:

$$\alpha_{\gamma} = 3.573 + 0.033x^{\gamma}. \tag{1}$$

The rectangular tensile specimens (width 5 mm, thickness 1.5 mm, and gauge length 15 mm) were prepared along the rolling direction. Since the background hydrogen concentration in the uncharged specimens is very low, only approximately 0.14 ppm, this not enough to observe the obvious hydrogen embrittlement phenomenon [6]. More hydrogen atoms were introduced intentionally by the electrochemical precharging method. At first, the surface of each specimen was carefully ground using very fine abrasive paper to eliminate the possible scratches or grooves, and then the specimen was subjected to the electrochemical precharging at different times. The precharging was carried out in a mixture solution of 0.1 mol/L NaOH and 1 g/L thiourea with the current density of 10 mA/cm^2. To ensure that only the gauge sections of the specimens were charged with hydrogen, the surfaces of the other sections were pre-coated with paraffin in advance. After the precharging, a slow strain rate test was conducted using a Zwick / Roell Z 020 machine with the constant strain rate of $1 \times 10^{-5}\ s^{-1}$. The index of relative susceptibility to hydrogen embrittlement (HEI) of the specimen was determined by measuring the relative elongation (δ) or reduction area (RA) loss of the samples, expressed as [6]:

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

$$RA_{\text{loss}}(\%) = \frac{RA_{\text{air}} - RA_{\text{charged}}}{RA_{\text{air}}} \times 100\%. \tag{3}$$

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

The electrochemical permeation method was applied to obtain the apparent diffusion coefficient of hydrogen in the specimen using the break-through method (D_b, m^2/s) and the time-lag method (D_l, m^2/s), as well as the apparent subsurface hydrogen concentration (C_b, wt ppm) using the "break-through time" method, respectively. Detailed descriptions can be found in references [6,20] and the main equations are:

$$D_b = \frac{L^2}{150.3tb}, \tag{4}$$

$$D_l = \frac{L^2}{6t_l}, \tag{5}$$

$$C_b = \frac{I_{\infty}L}{FD_b} \times \frac{M_H 10^6}{\rho_{Fe}}, \tag{6}$$

where L is the thickness of membrane (m), t_b is the break-through time (s); t_l is the time-lag (s) obtained by noting the time at which $I = 0.63\ I_{\infty}$, where I and I_{∞} are the permeation rate and steady state permeation rate (A/m^2), respectively. In addition, F is the Faraday constant (C/mol), M_H is the hydrogen molar mass (g/mol) and ρ_{Fe} is the iron density (g/m^3).