international journal of hydrogen energy XXX (2018) i-10



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Role of microstructure on electrochemical hydrogen permeation properties in advanced high strength steels

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ARTICLE INFO

Article history: Received 31 January 2018 Received in revised form 25 April 2018 Accepted 29 April 2018 Available online xxx

Keywords: Retained austenite Phase interfaces Hydrogen diffusion Trapping sites density Steels

ABSTRACT

The hydrogen permeation process in steels is closely associated with the microstructure of steels that greatly affect hydrogen trapping and hydrogen diffusion behaviors. In this study, the electrochemical hydrogen permeation experiment using a modified Devanathan-Stachurski (D-S) cells was employed to evaluate the hydrogen permeation properties in advanced high strength steels with four types of microstructures (from single phase, dual phase to complex phase). Results showed that both phase interfaces and retained austenite (RA) could act as the trapping sites for hydrogen and consequently reduced the hydrogen trapping behaviors depended on its morphology. Finally, the lattice diffusion coefficient (D_L) in each steel was determined and the correlations between the microstructure in steels and hydrogen evolution reaction (HER) kinetics were also investigated.

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Introduction

The development of advanced high strength steel (AHSS) is important and necessary for the automobile industry since it can effectively light the weight of automobile that reaches the purposes of energy conservation and emission reduction [1,2]. However, a notorious phenomenon called as hydrogen embrittlement (HE) heavily affects the durability of steels and especially AHSS since it generally gets more serious with increasing the strength of steels. A lot of effort has been devoted to investigate the correlations between the microstructures and hydrogen, for the intention of revealing the mechanism of HE in AHSS [3–8]. It is a crucial step to understand the diffusion and trapping of hydrogen in steels because the diffusible hydrogen is generally considered as one of main factors inducing HE in steels [9].

At current, electrochemical permeation technique using a unique equipment developed firstly by Devanathan and Stachurski [10], has been widely applied to investigate the influence of microstructure on hydrogen permeation in different

Please cite this article in press as: Zhou P, et al., Role of microstructure on electrochemical hydrogen permeation properties in advanced high strength steels, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.04.241

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nttps://doi.org/10.1016/j.ijnydene.2018.04.241

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types of steels, such as X70 [11,12], X80 [13], X100 [14] pipeline steels, stainless steel [15]. The application of this technique in AHSS has been also reported in many studies. For example, L. Qinglong et al. [16] compared the hydrogen permeation properties between some kinds of commercial dual-phase (DP) and quenching & partitioning (QP) steels, and observed a remarkable difference of around one order of magnitude in the lattice diffusion coefficient between DP ($\sim 10^{-6}$ cm² s⁻¹) and QP steel ($\sim 10^{-7}$ cm² s⁻¹). By the way of electrochemical permeation, O. Kazum et al. [17] measured the hydrogen diffusion coefficient in the nanostructured bainitic steel to be around $\sim 10^{-8}$ cm² s⁻¹. Whereas, it was observed that hydrogen diffusion in twinning-induced plasticity (TWIP) steel (~10⁻¹¹ cm² s⁻¹) at room temperature is generally lower by 3-4 orders of magnitude than other high-strength steels mentioned above [18]. It thus indicates that the diffusion of hydrogen is dramatically influenced by the microstructure of steels including grain boundaries, interfaces, dislocations vacancies, microvoids and precipitates [9,15,19]. Since such features often have stronger interaction with hydrogen than the lattice does, consequently, they can play as trapping sites to weaken the mobility of hydrogen in steels. The microstructure in AHSS is complicated, including single phase e.g. full martensitic steel (martensite), dual phase e.g. DP steel (ferrite and martensite) and complex phase e.g. QP steel (ferrite, martensite and austenite) [20], however, few was reported to investigate the effect of phase interfaces on hydrogen diffusion and trapping in steels.

In addition, the effect of retained austenite (RA) on hydrogen diffusion and trapping is also necessary to investigate and discuss. It is well-known that retained austenite (RA) plays an important role in some high-strength steels such as transformation induced plasticity (TRIP) and QP steels, where the phase transformation from RA to martensite (M) not only enhances the plasticity of steels but also provides a good work hardening effect at higher strain level [16,21]. However, the role of RA on HE susceptibility is still contested due to the contradictory results. In general, RA is considered as the trapping sites to hinder hydrogen mobility due to its low diffusion coefficient and high hydrogen solubility. Furthermore, it also has been proposed that austenite/martensite (or γ/α) interface can act as a strong trapping sites [9,22]. Accordingly, some studies proved that the HE resistance could be enhanced by RA as the beneficial traps [23,24]. Oppositely, the deteriorated effect of RA on the HE resistance was also found since the fresh martensite transformed from RA possessed the most negative resistance to HE and a detrimental hydrogen source was provided simultaneously to promote the nucleation and growth of crack [16,25]. Besides, it was also demonstrated that γ/α interface was the preferential position where the transgranular crack initiated [23]. Therefore, it is evident that the nucleation and growth of crack are closely associated with the hydrogen trapping in steel particularly in RA phase. In QP steel, RA has two types of morphologies: one is the filmy type surrounded by the martensite laths and the other is the blocky type situated within ferrite or adjacent to the martensite constituents. Our previous study [25] demonstrated that the HE susceptibility of QP steel could be suppressed by improving the stability of RA and the morphology of RA plays a dominant role in HE susceptibility of steels. However, the correlations between the detailed influence of RA on hydrogen diffusion and its morphology has never been investigated and clarified before, which will be one of main intentions in this work.

In this present study, four types of steels with different microstructures including one single phase, two dual phase and one complex phase were prepared by heat-treatment and their hydrogen diffusion and trapping behaviors were investigated by electrochemical hydrogen permeation method. Furthermore, it has been proposed that the surface features of materials can affect the hydrogen evolution reaction (HER) kinetics during polarization process [26,27], for example, the galvanized coating enhanced the HER kinetics whereas nickelbased coatings slowed it [28]. Thus, it is of interest what the impact of different microstructures on HER kinetics will be, which will be also investigated as an additional aim.

Experimental procedure

Materials and heat-treatments

A kind of commercial quenching & partitioning (QP) steel, of which nominal composition is 0.22C-1.40Si-1.80Mn, was selected as the substrate and designated as "as-received QP". As-received QP contains three types of phases, such as martensite (M), ferrite (F) and retained austenite (RA) (including two types of morphologies: filmy and blocky), as shown in Fig. 1(d). Subsequently, three heat-treatment routes were applied to obtain others types of steels. Firstly, to obtain a single martensite phase microstructure, the as-received QP was completely austenitized at 900 °C for 10 min and then was quenched in water to room temperature, which was titled as "QP-900°C-WQ". Secondly, the as-received QP was intercritical annealed at the temperature of 760 °C for 10 min following by quenching in oil to room temperature, and it was titled as "QP-760°C-OQ". Thirdly, the QP steel was quenched at 310 °C for 10 s after completely austenitizating at 900 °C for 10 min, following that was partitioning at 450 °C for 30 s. The last step was quenching in water to room temperature. Such prepared sample was titled as "QP-QP" in this study. The characterization of all the prepared samples was presented and discussed below.

The microstructure characterization of materials

X-ray diffraction (XRD, Rigaku, Japan) was applied to characterize the microstructure in these four types of steels and to measure the volume fraction of RA for QP-QP and as-received QP especially. In addition, samples were etched with 4% nital solution and then characterized by the optical microscopy (OM, ZEISS, Germany) and scanning electron microscopy (SEM, Tescan, Czech). In order to examine the filmy type of RA in steels, Transmission electron microscopy (TEM, JEOL, Japan) was utilized.

Galvanostatic hydrogen permeation experiments

In hydrogen permeation experiment, the samples with the original size of around 0.7 mm \times 15 mm \times 50 mm were

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