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# Determination of the Critical Plastic Strain-Induced Stress of X80 Steel through an Electrochemical Hydrogen Permeation Method

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ABSTRACT

The determination of critical plastic strain-induced stress ($\sigma_{cr}$) is significant to clarify the influence of stress level on an environmental fracture. The $\sigma_{cr}$ of high strength pipeline steel is difficult to define precisely based on conventional stress-strain curve. Hydrogen permeation behavior is sensitive to change in dislocations induced by plastic strain. Hence, a method of determining the $\sigma_{cr}$ of X80 steel is introduced by conducting electrochemical permeation experiments under slow-strain-rate tension. Hydrogen permeation current density ($i_H$) increases and then decreases with increased stress level within $R_{t0.5}$ (0.5% total extension). The stress at $i_{H,max}$ corresponds to $\sigma_{cr}$. Prior to $\sigma_{cr}$, the effective diffusion coefficient of atomic hydrogen $D_{eff}$ is reversible. Once $\sigma_{cr}$ is exceeded, $D_{eff}$ becomes irreversible. Binding energy $E_B$ of new hydrogen traps emerging during tension from 60% $R_{t0.5}$ to 90% $R_{t0.5}$ is close to that of dislocations in steel, which indicates that plastic deformation occurs in this tension stage. For X80 steel, the 95% confidence interval of $\sigma_{cr}$ ranges from 62% to 65% $R_{t0.5}$.

## 1. Introduction

Steel pipelines are widely used to transport oil, gas, water, and multiphase medium in onshore and offshore applications [1,2]. These transmission media are often corrosive. The safety of pipelines is threatened by environmental fractures, such as stress corrosion [3–5] and corrosion fatigue [6–8], under the combination action of residual, working, and/or environmental stress together with corrosive environment. Strain induced by stress within a metal is either elastic or plastic. Elastic strain is observed as a distortion of the crystal lattice, while plastic strain is observed by the presence of dislocations (the displacement of part of the crystal lattice). According to mechanochemical theory [9], elastic and/or plastic deformation can change electrode potential. Moreover, the value of the electrode potential is directly related to corrosion tendency of materials. Elastic strain has less impact on corrosion behavior of metallic materials [10], whereas plastic strain significantly influences corrosion [11,12]. Plastic strain causes multiplication, tangle, and dislocation reaction, as well as change surface activity and corrosion potential [11], and subsequently the changes of potential field influence nucleation of pits [13] in most active sites. Stress concentration at the bottom of pits could facilitate plastic deformation. Microcracks are then formed when local plastic deformation reaches a certain level [14,15]. The main crack initiation mechanism is pit-to-crack transition [14,16,17]. The size and shape of plastic zone are important in understanding the evolution at the crack tip [18]. Thus, the determination of critical plastic strain-induced stress is significant to elucidate the influence of stress level on crack initiation and propagation of environmental fracture.

Conventionally, critical plastic strain-induced stress is known as the proportional limit. The usual method of estimating this limit is to measure the departure of the stress–strain curve from linearity. In Fig. 1(a), the stress at point A defines the proportional limit. However, no evident yield stage is indicated for many metallic materials including pipeline steels (see Fig. 1(b)). This issue challenges the determination of the proportional limit. In addition, a degree of uncertainty must be defined in relation to what constitutes departure. For grades not higher than X90 for pipeline steel, tensile tests are usually conducted to determine 0.5% total extension ($R_{t0.5}$) as yield strength [19]. However, a material at $R_{t0.5}$ already has a small amount of nonlinear tension and the corresponding plastic strain facilitates local corrosion and pit-to-crack transition. $R_{t0.5}$ is not the critical plastic strain-induced stress, and new techniques that are sensitive to the presence of plastic strain should be developed.

The generation, movement, and storage of dislocations govern plastic deformation [20]. In the early stages of plastic deformation

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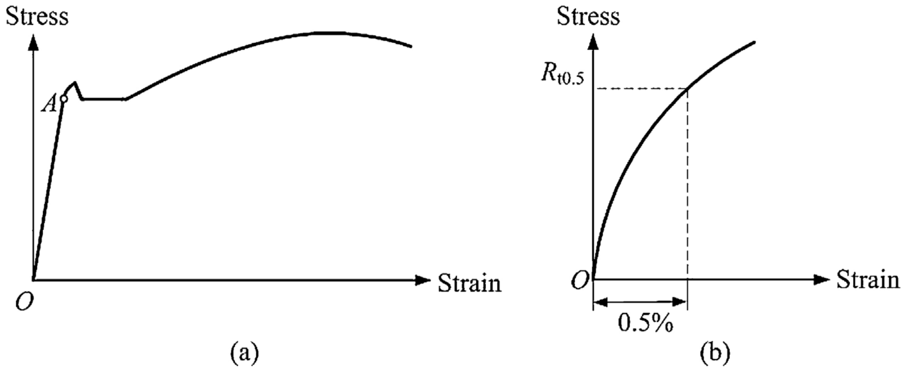

**Fig. 1.** Typical stress vs. strain diagrams. (a) With yield stage and (b) without yield stage.

of materials, new dislocations generate by multiplication [21]. Diffraction in the transmission electron microscope (TEM) enables direct observation of dislocations [22] and the change in dislocations induced by applied stress can be studied by *in situ* deformation tests in the electron microscope [23]. These data are undoubtedly important for investigating the relationship between dislocation evolution and plasticity [24]. However, TEM is not recommended for a general statistical study because of its time-consuming sample preparation and analysis, which limit the number of areas that could be studied. X-ray diffraction [25,26] or neutron diffraction [27] experiments capture the general statistical nature of the problem well but they tend to lack spatial resolution. Moreover, establishing a loading device onto these sophisticated equipments is not easy, and the analysis of dislocation density requires expertise.

Dislocations are generally known as hydrogen traps [28,29], Hutchings and Turnbull confirmed that dislocations are reversible trap sites [30]. Therefore, dislocation multiplication induced by plastic deformation is expected to influence hydrogen transport. Normally, dislocations can reduce hydrogen diffusion coefficient [31]. Li [32] found that 1% pre-strain could decrease effective diffusion coefficient of high strength steel, which was attributed to increasing dislocations. Plastic deformation results in the change of dislocation, and dislocation change influences hydrogen permeation behavior. Therefore, elastic-plastic transition could be determined by monitoring the change of hydrogen permeation.

Various techniques are developed to measure hydrogen transport, including permeation foils in gas or electrochemical cells, outgassing experiments by gas analysis methods, uptake or saturation curve experiments, radioactive radiotracers, Matano method, internal friction measurements, and scanning kelvin probe voltage mapping [33]. In electrochemical hydrogen permeation experiments, hydrogen atoms diffuse from the charging side of a Devanathan-Stachurski cell through a metallic specimen that is measured by the oxidizing current density in the detection side. This established method [34] makes easy to evaluate hydrogen uptake, permeation, and transport because this measurement is direct and easy to conduct. In addition, electrochemical hydrogen detection method is more efficient than gas stream measurement technique [35].

Kim conducted electrochemical hydrogen permeation measurements under various loading conditions and found that dislocation multiplication could decrease permeation current density [36] and slow down permeation rate [37]. We hereby speculate that the elastic-plastic transition stress could be determined by the change of hydrogen permeation current during tensile testing. The main difference between elastic and plastic strain is whether the strain change could return to its original state after releasing the applied stress. Therefore, the reversibility of change in hydrogen diffusion coefficient induced by loading and unloading could be used as an indicator of the strain state. Furthermore, determining the value of binding energy of hydrogen traps could be helpful to justify if new emerging traps are dislocations.

In this study, *in situ* observation of the change in hydrogen permeation current was evaluated under slow-strain-rate tension (SSRT) to find the suspected elastic-plastic transition stress. The change of hydrogen diffusion coefficient with applied stress, reversibility of this change, and binding energy of hydrogen with new emerging trapping sites were studied by conducting electrochemical hydrogen permeation measurements under various preset loading and unloading conditions. All these methods helped determine the critical plastic strain-induced stress. Finally, a simple method was proposed to determine the critical stress that initiates plastic strain by monitoring the change in permeation current during SSRT process.

## 2. Experimental

### 2.1. Materials

This study used X80 steel, which contains 0.070% C, 0.200% Si, 1.830% Mn, 0.007% P, 0.001% S, 0.230% Cr, 0.260% Mo, 0.033% Ni, 0.071% Nb, 0.001 V, 0.015 Ti, 0.012 Cu, 0.0002 B, and 0.040 Al and Fe balance. The microstructure was investigated at different scales by using a Leica DM2500M optical microscope and a Tecnai F30 TEM. As shown in Fig. 2(a) and (b), X80 steel is characterized by ferrite (F) and bainite (B) with high density of dislocations. *In situ* TEM mechanical observation results show that X80 steel has the combination of strength and ductility properties owing to the cooperative deformation mechanism between soft F and hard B [38].

Large, flat tensile samples (gauge length, 40 mm; section width, 26 mm; thickness, 0.7 mm) were used to investigate hydrogen permeation behavior during tensile straining. Prior to the tests, all steel specimens were ground to 2000-grade emery paper on both sides and cleaned with distilled water and absolute ethyl alcohol.

### 2.2. Electrochemical permeation experiments

#### 2.2.1. Under SSRT

Electrochemical hydrogen permeation tests [34] were conducted by fixing a specimen on a tensile-testing machine between the two compartments of a Devanathan–Stachurski cell subjected to 303 ± 0.5 K thermostat (Fig. 3). Cathodic polarization was performed in the hydrogen charging compartment from deaerated 3.5 wt.% NaCl + 0.1 wt.% $Na_2S$ solution at −1100 mV (vs. SCE) by a PS–1 potentiostat. Anodic polarization was performed in the