Hydrogen Permeation Property and Hydrogen Embrittlement Susceptibility of Pipeline Steel with Oxide Film

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Keywords: Hydrogen embrittlement, Hydrogen permeation, Oxide film.

Abstract. In this study, the oxide film on X80 steel was fabricated to decrease hydrogen embrittlement of pipeline steel. The microstructures and mechanical properties in 10MPa hydrogen gas and hydrogen permeation properties were investigated. The phase structure of oxide film was mainly composed of Fe\textsubscript{3}O\textsubscript{4}. With the increasing of oxidation temperature, surface oxygen content improves gradually. Oxide film plays an important role in resisting hydrogen penetrating. Hydrogen diffusion coefficient decreases from 38.81\times10^{-7} \text{cm}^2 \text{s}^{-1} to 1.26\times10^{-7} \text{cm}^2 \text{s}^{-1} for oxidation at 450 °C. The plastic deformation increases obviously after oxidation. HEI decreases from 40.96% to 11.61% for oxidation at 450 °C.

Introduction

Decreasing the emission of CO\textsubscript{2} is currently a global concerned serious problem. Scientists continually explore new energy to solve the problem. Hydrogen is a clean-burning fuel to replace fossil fuel\textsuperscript{[1]}. Hydrogen mainly exists in the form of H\textsubscript{2}. Transporting hydrogen gas through pipelines is the most effective way relative to other transportation methods\textsuperscript{[2,3]}. Hydrogen embrittlement of pipeline steels is an extremely important topic which reduces mechanical properties of pipeline steel\textsuperscript{[4]}. Hydrogen embrittlement increases with alloy strength\textsuperscript{[5]}.

Technology of hydrogen barrier coatings was proposed to decrease hydrogen diffusion and hydrogen embrittlement\textsuperscript{[6]}. The hydrogen barrier coatings are mainly prepared by surface oxidation, physical and chemical deposition on the base material\textsuperscript{[7-9]}. The results of Qin showed diffusion of hydrogen in TiO\textsubscript{2} was three orders of magnitude lower than that in titanium\textsuperscript{[10]}. Al\textsubscript{2}O\textsubscript{3} coating on titanium protects base material in high pressure hydrogen atmosphere\textsuperscript{[11]}\textsuperscript{[12,3]}. Cr\textsubscript{2}O\textsubscript{3} and Er\textsubscript{2}O\textsubscript{3} coatings also have good properties of hydrogen permeation resistance\textsuperscript{[12-13]}. Su\textsuperscript{[14]} prepared passive films on iron by anode passivation method. The hydrogen transport through the passive film was hindered. The oxide film was prepared on AISI430 steel by applying high-temperature oxidation\textsuperscript{[15]}. Its surface oxide film was rich in Cr. It impeded the adsorption of hydrogen and increased elongation in hydrogen environment from 15% to 24%. Physical vapor deposition and chemical vapor deposition technologies are difficult to applied on long-distance transport hydrogen pipeline steel. Oxide film is easily prepared on pipeline steel. And many studies have shown they are effective to decrease hydrogen diffusion. However, there are lack of research on the relationship between pipeline steel oxide film and its hydrogen permeation properties.

In this study, the oxide film on X80 steel was prepared by high temperature oxidation. The mechanical properties of X80 steel with and without oxide film in hydrogen environment were tested. The effects of oxide film on hydrogen permeation and hydrogen embrittlement susceptibility were analyzed.
Experimental

X80 steel was selected as the base material. Its chemical composition contains 0.06% C, 1.81% Mn, 0.27% Si, 0.002% S, 0.011% P, 0.28% Cu, 0.07% Nb, 0.31% Mo, 0.3% Ni, 0.02% Cr, 0.005% N, 0.015% Ti, 0.01% Al and balance Fe. The base material was machined as 10mm×10mm×10mm for microstructure analysis. The surfaces of the material were ground to with SiC papers to 1000 grade and were polished. They were oxidized in a chamber furnace at 350 °C for 1h, 450 °C for 1h, 600 °C for 1h. The microstructure and chemical composition were analyzed by Hitachi an S-3400N scanning electron microscope (SEM) and a Horiba Emax-350 energy dispersive spectrometer (EDS), respectively. The phase structure of the oxide film were conducted by the analysis of X-ray diffractometer (XRD).

Hydrogen permeation test were conducted to test the hydrogen barrier permeability of the oxide film by traditional Devnathan–Stachurski double electrolytic cell\[^{[16]}\]. The corresponding sample was \(\varphi24\) mm×2 mm. After oxidation, one side of the sample was ground to remove the film with 600 grade SiC papers. This side was platted nickel to reduce the interference of background current and was placed toward anodic cell. Cathode cell and anodic cell were filled with 0.1mol/L NaOH. Subsequently, electrochemical hydrogen permeation test was conducted with charging hydrogen current density of 1mA/cm\(^2\). The hydrogen permeation current was measured until it reached a steady state.

Slow strain rate tensile test in 10MPa high-pressure hydrogen atmosphere were conducted to test the effect of oxide film on hydrogen embrittlement. The test were run at strain rate of \(10^{-5}\) s\(^{-1}\). The tensile strength, the elongation of fractured specimen, and the reduction of cross section were obtained from the tensile test. The index of hydrogen embrittlement index (HEI) was calculated by equation (1).

\[
\text{HEI} = \frac{\varphi_{N_2} - \varphi_{H_2}}{\varphi_{N_2}} \times 100\%
\]

where \(\varphi_{N_2}\) and \(\varphi_{H_2}\) are the reduction of cross section in nitrogen gas and hydrogen gas, respectively. The index of hydrogen embrittlement means the decreased plasticity due to hydrogen environment. The higher of HEI indicates improved hydrogen embrittlement.

Results and Discussion

Phase Structures and Microstructure of the Oxide Films

Figure 1 shows XRD patterns of the oxide films of X80 steel. The base material X80 steel was low carbon microalloyed steel, which was mainly composed of ferrite. No phase structure of iron oxide was detected for 350 °C oxidation. It means the content of oxide film is too small to be detected. A new peak at 35.4° was found for 450 °C oxidation. It was a diffraction peak of Fe\(_2\)O\(_3\) phase structure. With the increasing of oxidation temperature, the intensity of 35.4° peak increases and 62.5° peak appears. It indicates increased Fe\(_2\)O\(_3\) phase content. The new Fe\(_3\)O\(_4\) phase was found for oxidation at 600°C.

![Figure 1. XRD patterns of X80 before and after oxidization.](image-url)
Figure 2 shows surface morphologies of X80 steel oxidized at different temperature. It can be seen that the surface morphologies are smooth after oxidization of 350°C and 450°C. Their oxide films are dense and a little pores. After oxidation at 600 °C, the surface morphology is obviously different from that of 350°C and 450°C oxidation, showing wormlike structure and uneven surface. The EDS results of area A and area B in Figure 2c show that the contents of O and Fe are same, whereas area B is rich in Si and Mn elements.

![Figure 2. Surface morphologies of X80 steel oxidized at different temperature.](image)

Figure 2. Surface morphologies of X80 steel oxidized at different temperature. (a) 350°C, (b) 450°C, (c) 600°C

Figure 3 shows cross-section morphologies and oxygen distribution curves of X80 with oxide film. The oxide films are closely combined with the substrate for 350°C oxidation and 450 oxidation. However, there is cracks for 600°C oxidation. With the increasing of oxidation temperature, surface oxygen content improves gradually. The thickness of oxide film is 0.53 μm, 1.61 μm and 1.02 μm for oxidation at 350 °C, 450 °C, 600 °C, respectively. The thickness of oxide film at 600 °C oxidation is less than that at 450 °C oxidation. It is due to the oxide film falling off at 600 °C oxidation.

![Figure 3. SEM morphologies of the cross-section of the oxide films (a) 350°C, (b) 450°C, (c) 600°C, (d) oxygen element ditribution curves at 350 °C, (e) oxygen element ditribution curves at 450 °C, (f) oxygen element ditribution curves at 600 °C.](image)

Figure 3. SEM morphologies of the cross-section of the oxide films (a) 350°C, (b) 450°C, (c) 600°C, (d) oxygen element distribution curves at 350 °C, (e) oxygen element distribution curves at 450 °C, (f) oxygen element distribution curves at 600 °C.

**Hydrogen Permeation Properties of X80 Steel with and without Oxide Film**

Hydrogen permeation curves of X80 steel with and without oxide film are shown in Figure 4. Hydrogen diffusion coefficient (D) was calculated by Fourier method which is shown in equation 2.

\[
\ln\left(1 - \frac{I_t}{I_\infty}\right) = \text{const} - \frac{\pi^2 D t}{L^2}
\]

where \(I_\infty\) and \(I_t\) means the steady-state current and the current at t time, respectively. L indicates the thickness of the specimen. The slope of \(\ln\left(1 - \frac{I_t}{I_\infty}\right)\) against \(\frac{\pi^2 t}{L^2}\) is diffusion coefficient D. The hydrogen diffusion coefficients are shown in Table 1. The hydrogen permeation current is 0 at the beginning of hydrogen permeation. H atom is produced on specimen in cathodic cell. Then H atom is
adsorbed on the specimen. It is difficult to monitor the time taken in the adsorption process. Fourier method is independent of the start time. So it is reliable to calculate hydrogen diffusion coefficient D.

Figure 4. Hydrogen permeation curves of X80 steel with and without oxide film.

(a) without oxide film, (b) 350°C, (c) 450°C, (d) 600°C

The steady-state current density is significantly reduced for X80 with oxide film. The current density after 600 °C oxidation is only 2.7% of the X80. Hydrogen diffusion coefficient is less than one tenth of that before oxidation. It decreases to $1.26 \times 10^{-7} \text{cm}^2 \cdot \text{s}^{-1}$ for 450 °C oxidation. The oxide film formed on the surface hinders H atom diffusion into X80 base material. Fe$_2$O$_3$ which is the main structure of oxide film is corundum-type structure. The crystal structure is the same as Al$_2$O$_3$ which is excellent material in restricting hydrogen diffusion. Fe$_2$O$_3$ in oxide film plays an important role in resisting hydrogen diffusion.

The process of H atom penetrating X80 with oxide film can be described as the following model shown in Fig 5. First, new produced H atom is adsorbed on the oxide film. Some adsorbed H atoms forms H$_2$, and leave surface. The others diffuse into oxide film and reach the interface between the oxide film and base material. Subsequently, H atoms are adsorbed on the base material. Then they penetrate base material and reach the anode side, and becomes H$^+$. All of the above processes are continuous. Any process may be the rate control step of hydrogen permeation. Above analysis shows hydrogen permeation speed of X80 steel with oxide film is decreased. The processes of H adsorption and diffusion in X80 with oxide film is different from that of X80 without oxide film. The oxide film decreases hydrogen penetrating current and hydrogen diffusion coefficient.

Table 1. Hydrogen permeation parameters for X80 steel with and without oxide film.

| T / °C | Before oxidation | 350°C | 450°C | 600°C |
|-------|------------------|-------|-------|-------|
| $I_\infty / \mu \text{A} \cdot \text{cm}^{-2}$ | 4.67 | 1.73 | 1.75 | 0.13 |
| $D / 10^{-7} \text{cm}^2 \cdot \text{s}^{-1}$ | 38.81 | 2.07 | 1.26 | 3.72 |
Figure 5. The process of H atom diffusion into X80 with oxide film.

Mechanical Properties of X80 Steel with and without Oxide Film

The mechanical properties of X80 with and without oxide film in 10MPa hydrogen environment is shown in Table 2. It shows that tensile strength of X80 steel slightly decreases after oxidation. The reduction of area and the elongation after fracture increases obviously. And HEI decreases which is 11.61% for 450 °C oxidation. Previous research indicates hydrogen induced fracture is not easy to occur when HEI the material is less than 25% [17]. It illustrates X80 steel with oxide film recovers new deformation ability in hydrogen gas.

Table 2. The mechanical properties of X80 with and without oxide film.

| T /°C | Environment | Rm/MPa | A/%  | Z/%  | HEI/% |
|-------|-------------|--------|------|------|-------|
| Before oxidation | N₂ | 700.7 | 28.28 | 74.27 | ~     |
| Before oxidation | H₂ | 700.96 | 21.31 | 43.85 | 40.96 |
| 350   | H₂ | 700.14 | 4.52  | 47.95 | 35.33 |
| 450   | H₂ | 665.83 | 7.77  | 65.55 | 11.61 |
| 600   | H₂ | 671.81 | 7.66  | 52.53 | 28.12 |

SEM images of the fracture surfaces of X80 before and after 450 °C oxidation are shown in Figure 6. The overall morphology of X80 without oxide film is relatively even and perpendicular to the direction of external tensile load compared with that of X80 with oxide film. Obvious necking deformation is found for X80 with oxide film. The cracks initiate from surface. There are secondary cracks and quasi cleavage facets in detail of area of A. They are typical brittle fracture characteristics. Deformed dimple and secondary cracks are found in detail of area B. Dimple is the characteristics of ductile fracture. It shows oxide film increases plastic deformation ability of X80 steel.

Figure 6. Fractures morphologies of X80 steel tested in hydrogen gas. (a) overall morphology for X80 (b) overall morphology for X80 at 450 °C oxidization (c) detail of area A (d) detail of area B.
Conclusions

In this study, the oxide film on X80 steel was fabricated. The microstructure and mechanical properties in 10MPa hydrogen gas and hydrogen permeation properties were investigated. The following conclusions can be drawn:

1. Oxide phase structure of oxide film was Fe₂O₃ for oxidization at 450 °C.
2. Oxide film plays an important role in resisting hydrogen penetrating. Hydrogen diffusion coefficient decreases from 3.81×10⁻⁷ cm²·s⁻¹ to 1.26×10⁻⁷ cm²·s⁻¹ for oxidation at 450 °C.
3. The plastic deformation increases obviously after oxidation. HEI decreases from 40.96% to 11.61% for oxidation at 450 °C.

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