Full Length Article

Optimizing hydrogen permeation properties of WS$_2$-Ni composite coatings on pipeline steel for improved hydrogen protection

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A R T I C L E   I N F O

Keywords:
- Tungsten disulfide
- Hydrogen barrier
- Hydrogen embrittlement
- Coating
- Electrodeposition

A B S T R A C T

Tungsten disulfide (WS$_2$) has broad applications due to its unique molecular structure and outstanding physicochemical properties. In particular, the physical barrier properties of WS$_2$ make it suitable to act as barriers against hydrogen. Herein, WS$_2$-Ni composite coatings are prepared by electrodeposition to mitigate hydrogen-induced damage of X70 pipeline steel. The influence of the WS$_2$ concentration on the hydrogen resistance of coating is assessed by electrochemical hydrogen permeation test, hydrogen adsorption simulation, slow strain rate tensile test (SSRT), and fracture analysis. As the WS$_2$ concentration increases, the distributions of WS$_2$ in the coatings transition from sparse to uniform and then agglomeration, while the grain size of Ni decreases initially and then decreases. These microstructural changes impact the hydrogen adsorption sites and diffusion paths, leading to a non-linear relationship between the hydrogen permeation resistance and WS$_2$ concentration. This similar concentration dependence is also observed from the hydrogen embrittlement (HE) resistance of coatings, suggesting that enhancing the hydrogen permeation resistance can improve the HE resistance. This study highlights the great potential of WS$_2$ as an effective barrier against hydrogen permeation, and the results provide insights into the hydrogen protection mechanism of pipeline steel.

1. Introduction

Hydrogen is attractive as a renewable and pollution-free energy source to alleviate resource shortages and environmental pollution [1–6]. The hydrogen energy industry covers five major sectors, namely hydrogen production [7], hydrogen storage [8], hydrogen transportation [9], hydrogen refueling [10], and hydrogen utilization [11]. In order to link production to storage, refueling, and utilization, hydrogen transportation plays a significant role. However, conventional steel pipelines are vulnerable to hydrogen damage, frequently leading to plastic loss [12–14]. Hydrogen barrier coatings can mitigate hydrogen permeation without compromising the inherent properties of the bulk materials and have attracted industrial interest [15]. Although different types of hydrogen barrier coatings, such as oxides [16–19] and non-oxides [20–22], have been proposed, traditional hydrogen barrier coatings continue to be plagued by the susceptibility to cracking, complex preparation processes, poor thermal stability, and poor bonding. Recently, two-dimensional nanomaterials have garnered significant research interest [23]. For example, Fan et al. [24] have observed that graphene coatings can resist hydrogen permeation, and the hydrogen permeability of the coated specimens decreases by 50%. Checcetto et al. [25] have found that boron nitride films retard hydrogen diffusion and inhibit hydrogen permeation, and Shi et al. [26] have investigated the resistance to hydrogen embrittlement (HE) for pipeline steel coated with Mxene and shown that the hydrogen permeability is one-third of that of the substrate. Tungsten disulfide (WS$_2$) is a promising hydrogen barrier material due to its unique “sandwich” structure, outstanding molecular sieve properties, and excellent physicochemical properties [27–29]. Nevertheless, the application of WS$_2$ in hydrogen barrier coatings has not been intensively investigated, and the mechanism of WS$_2$ against hydrogen permeation is not well understood.

In this study, WS$_2$-Ni composite coatings with different WS$_2$ contents...
are prepared on X70 pipeline steel by electrodeposition. The microstructure and morphology of the coatings are characterized by field-emission scanning electron microscopy (SEM) and X-ray diffraction (XRD), and the hydrogen resistance is evaluated by electrochemical hydrogen permeation test, hydrogen adsorption simulation, slow strain rate tensile (SSRT) test, and fracture analysis. The effects of the WS$_2$ concentration and microstructure on the hydrogen permeation resistance and HE resistance are determined. The hydrogen permeation behavior and mechanism are explored to determine the optimal WS$_2$ concentration to prevent hydrogen damage.

2. Experimental details

2.1. Materials and specimen preparation

The X70 pipeline steel substrate was cut into rectangular sheets with dimensions of 50 mm $\times$ 30 mm $\times$ 1 mm, polished with sandpaper and abrasive paste to a mirror finish, cleaned ultrasonically with ethanol, and dried. Before electrodeposition, one side of the substrate was insulated and sealed with insulating adhesive to ensure single-side deposition. The preparation process of WS$_2$-Ni composite coatings is illustrated in Fig. 1. WS$_2$ was modified with cetyltrimethylammonium bromide (CTAB) to improve dispersion and then electrodeposition was carried out using a two-electrode system, in which the steel substrate was the cathode, a platinum sheet was the anode, and Ni-based plating solutions (250 g/L NiSO$_4$⋅6H$_2$O, 45 g/L NiCl$_2$⋅6H$_2$O, and 40 g/L H$_3$BO$_3$) doped with different concentrations of WS$_2$ (0 g/L, 3 g/L, 5 g/L, 7 g/L, and 9 g/L) was the plating solution. Electrodeposition was performed at a current density of 10 mA/cm$^2$ for 15 min at 25 ± 2°C.

2.2. Electrochemical hydrogen permeation evaluation

The electrochemical hydrogen permeation test was conducted to evaluate the hydrogen permeation resistance of the coatings using the Devanathan-Stachurski (D–S) cell [30]. As shown in Fig. 2, the D–S cell consisted of a cathode cell (hydrogen charging) and an anode cell (hydrogen detecting). The coated specimen was the working electrode, whereas the saturated calomel electrode and platinum plate were the reference and counter electrodes, respectively. The coated side of specimen was connected to the cathode cell filled with 0.2 mol/L NaOH and 3 g/L NH$_4$SCN, and the uncoated side of specimen was connected to the anode cell filled with 0.2 mol/L NaOH. Before the test, the uncoated side of the specimen was plated with Ni at a charging current density of 10 A/cm$^2$ for 5 min in a plating solution consisting of 250 g/L NiSO$_4$⋅6H$_2$O, 45 g/L NiCl$_2$⋅6H$_2$O and 40 g/L H$_3$BO$_3$. The background current density was reduced to less than 0.1 $\mu$A/cm$^2$ by imposing a constant potential of 0.2 V in the anodic cell. A constant current of 20 mA/cm$^2$ was then applied to the cathode cell to start the electrochemical hydrogen permeation test, and the hydrogen permeation current curves were obtained by the electrochemical workstation. The hydrogen diffusion coefficient $D$ and hydrogen permeability $J$ were calculated by the following equations [31]:

$$D = \frac{L^2}{15.3t_b} \quad (1)$$

$$J = \frac{i_p^\infty \times L}{F} \quad (2)$$

where $L$ is the thickness of the specimen, cm; $t_b$ is the breakthrough time, s; $i_p^\infty$ is the steady state current density, $\mu$A/cm$^2$; $F$ is Faraday’s constant (96,485C/mol).

2.3. Hydrogen adsorption simulation

The simulation was conducted by the CASTEP module in Material...
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The adsorption energy of hydrogen and WS₂ was calculated by the following equation:

\[ E_{\text{ads}} = E_{(H/WS₂)} - E_{(WS₂)} - \frac{1}{2}E_{(H₂)} \]  

(3)

where \( E_{(H/WS₂)} \) and \( E_{(WS₂)} \) represent the energy of the WS₂ with or without hydrogen adsorption (eV) and \( 1/2E_{(H₂)} \) is the energy of hydrogen (eV).

2.4. Slow strain rate tensile test

The mechanical properties of the coated specimens before and after hydrogen charging were determined by the SSRT test, and the susceptibility to HE was evaluated [32]. The SSRT test was carried out on the hydrogen compatibility machine (YYF-30E, Shanghai Bairoe Testing Instrument Co., Ltd., China) at a strain rate of \( 5 \times 10^{-5} \) s⁻¹. As shown in Fig. 4, the specimens for the SSRT test with a gauge length of 15 mm, gauge width of 2 mm, and thickness of 1 mm were cut from the coated specimens.

The hydrogen-charged specimens were pre-charged electrochemically in 0.2 mol/L H₂SO₄ with 3 g/L thiourea at a charging current density of 50 mA/cm² for 24 h. Before hydrogen charging, the surface of the specimen outside the gauge section of the coating side was covered with sealing mud to ensure that hydrogen charging occurred on the coating surface of the gauge section (Fig. 5). The ultimate tensile strength (UTS) was obtained from the stress-strain curves, and the total elongation (Elₜ) corresponding to the strain at failure was calculated from the data of the gauge length at failure. The reduction of area (RA) was used as the basis to evaluate the susceptibility to HE of coated specimens. The index of HE (RAₜₜₜₜₜₜₜₜ) was calculated by the following equation:

\[ RA_{\text{test}} = \frac{RA_{\text{HF}}}{RA_{\text{UHF}}} \times 100\% \]  

(4)

where RA₀ and RAₜₜₜₜₜₜₜ represent the RA of the uncharged and hydrogen-charged specimens, respectively.

2.5. Characterization

The modification of WS₂ was characterized by Zeta potential and particle size distribution tests using wet method with the test concentration of 0.1 g/L. The microstructure of the coated specimens and the fracture morphology of the tensile specimens were examined by SEM with an accelerating voltage of 2 kV and the magnification ranging from 200 x to 20 kx. The phase composition of the coated specimens was investigated by grazing incidence XRD with a scanning speed of 2°/min, a scanning step of 0.03°, a fixed incidence angle of 1° and a scanning angle range of 10°–90°.

Fig. 4. Dimensions of tensile specimens (mm).

Fig. 5. Schematic of the electrochemical hydrogen charging.

Fig. 6. Characterization results of WS₂ aqueous solution before and after modification: (a) Zeta potentials and (b) Particle size distributions.
3. Results

3.1. Characterization

WS$_2$ tends to form the agglomerate structure in the solution, which is difficult to disperse uniformly in the plating solution and have a serious impact on the controllability of electrodeposition. The characterization results of the WS$_2$ aqueous solution before and after modification are shown in Fig. 6. As shown in Fig. 6(a), the average potential of the WS$_2$ aqueous solution increases from $+0.7$ V to $+38.4$ V after modification, indicating that the combination of CTAB and WS$_2$ results in positive charges on the WS$_2$ surface. As shown by particle size distribution (Fig. 6(b)), an average particle size decrement of $56.85 \mu$m from $64.57 \mu$m to $7.72 \mu$m is observed after modification, possibly because the repulsive effect of the homogeneous charges between the modified WS$_2$ reduces agglomeration of WS$_2$.

Fig. 7 shows the XRD patterns of the composite coating at different WS$_2$ concentrations. The WS$_2$ content and the full width at half maximum of the Ni (111) peak of different composite coatings are calculated by the JADE analysis software. The results show that the WS$_2$ content increases from 0 % to 24.8 % as the WS$_2$ deposition concentration increases from 0 g/L to 9 g/L. In addition, the full width at half maximum of the Ni (111) peak for concentrations of 0 g/L, 3 g/L, 5 g/L, 7 g/L, and 9 g/L are 0.409, 0.455, 0.468, 0.463, and 0.451, respectively. According to the following Scherrer equation, it can be inferred that the smaller full width at half maximum reflects the larger grain size. Thus, it can be seen that the grain size of Ni shows a trend of decreasing and then increasing as the WS$_2$ deposition concentration increases.

$$D = \frac{K\gamma}{\beta \cos \theta}$$  \hspace{1cm} (5)

where $D$ is the grain size, nm; $K$ is the Scherrer's constant; $\gamma$ is the X-ray wavelengths, Å; $\beta$ is the full width at half maximum, rad; $\theta$ is the Bragg angle, degree.

Fig. 8 exhibits the surface morphology of the coated specimens with different WS$_2$ concentrations. As shown in Fig. 8(a), a granular morphology is observed from the pure Ni coating (0 g/L). Fig. 8(b) shows that the morphology may be caused by the difference in the grain size and poor structural compactness of the Ni layer. As the WS$_2$ concentration increases, sparsely distributed WS$_2$ is observed for 3 g/L (Fig. 8(c)). The structure of Ni layer tends to be denser, and the grain size of Ni becomes homogeneous (Fig. 8(d)). When the WS$_2$ concentration is 5 g/L (Figs. 8(e) and (f)), the amount of WS$_2$ in the composite coating increases, showing a uniformly distributed morphology. Moreover, the Ni grain size is further refined, and the structure of Ni layer becomes denser. However, an obvious accumulation of WS$_2$ is observed for 7 g/L, manifesting as a “honeycomb” stacking morphology (Fig. 8(g)). The grain size and structural characteristics of Ni tend to be stable under this condition (Fig. 8(h)). When the WS$_2$ concentration increases further to 9 g/L (Fig. 8(i)), severe WS$_2$ agglomeration is observed, thus affecting the
uniformity of WS<sub>2</sub>. The high-magnification characterization result (Fig. 8(j)) reveals that the grain size of the Ni layer increases as the crystallization of the Ni layer is affected by the excessive WS<sub>2</sub>. In summary, as the WS<sub>2</sub> concentration increases from 0 to 9 g/L, the composite coatings evolve from a sparse distribution that is uniformly dense to locally aggregated and then severely agglomerated, while the Ni grain size decreases and then increases.

Fig. 9 displays the cross-section morphology of the coated specimens at different WS<sub>2</sub> concentrations. The results show that the cross-section of the coated specimens is flat with no obvious holes and cracking defects in the interior. In addition, the thickness of the composite coating doped with WS<sub>2</sub> ranges from 45 to 48 µm, which is increased significantly compared with the Ni coating. This may be due to the addition of WS<sub>2</sub> occupying the internal space of the composite coating.

### 3.2. Hydrogen permeation

The electrochemical hydrogen permeation results are shown in Fig. 10 and the hydrogen permeation parameters calculated by Eqs. (1) and (2) are presented in Table 1. The permeation current of the uncoated substrate shows the highest steady-state current density with D and J reaching 7.34 × 10^−7 cm²·s<sup>−1</sup> and 1.73 × 10^−5 mol·(cm·s)<sup>−1</sup>, respectively. The permeation current of the Ni-coated specimens (0 g/L) is similar to that of the substrate with the calculated D and J close to those of the uncoated substrate, implying that the pure Ni coating prepared in this study cannot effectively hinder the permeation of hydrogen atoms. The hydrogen permeation time of the composite coating deposited with 3 g/L is extended to 1500 s, which is 1000 s later than that of the uncoated substrate, while D and J of the specimen separately decrease to 2.79 × 10<sup>−7</sup> cm²·s<sup>−1</sup> and 8.88 × 10<sup>−6</sup> mol·(cm·s)<sup>−1</sup>, respectively. When the WS<sub>2</sub> concentration is further increased to 5 g/L, the composite coating demonstrates the best hydrogen permeation resistance with D and J reduced to 2.58 × 10<sup>−7</sup> cm²·s<sup>−1</sup> and 5.10 × 10<sup>−6</sup> mol·(cm·s)<sup>−1</sup>, which are 3 times and 3.5 times lower than those of the uncoated substrate, respectively. However, the further increase of the WS<sub>2</sub> concentration deteriorates the hydrogen permeation resistance. D and J of the composite coating deposited with 7 g/L increase to 3.37 × 10<sup>−7</sup> cm²·s<sup>−1</sup> and 7.64 × 10<sup>−6</sup> mol·(cm·s)<sup>−1</sup>, while D and J of that deposited with 9 g/L increase further to 3.67 × 10<sup>−7</sup> cm²·s<sup>−1</sup> and 1.18 × 10<sup>−5</sup> mol·(cm·s)<sup>−1</sup>. Interestingly, it can be found that the evolution trend of permeation curve of the uncoated substrate is not consistent with that of the coated specimens. This may be explained as follows. As permeation proceeds, the progressive increase in the hydrogen concentration on the surface of the uncoated substrate results in the occurrence of surface stress, which leads to the development of defects, such as microcracks and blisters [33]. And the defects play the role of hydrogen trap, which can capture the hydrogen atoms entering the substrate [34]. Therefore, it can be observed that the permeation curve descends. As the defect gradually reaches the hydrogen absorption saturation, the hydrogen trap effect of defect diminishes, which leads to the rising of permeation curve. Differently, WS<sub>2</sub>-Ni coating can effectively hinder the permeation of hydrogen atoms into the substrate and reduces the hydrogen concentration on the surface of the substrate. This may avoid the generation of defects that can become hydrogen traps. As a result, the descend trend is not observed in the hydrogen permeation curve of coated specimens.

### Table 1: Hydrogen permeation parameters of WS<sub>2</sub>-Ni composite coatings.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>t&lt;sub&gt;b&lt;/sub&gt; (s)</th>
<th>t&lt;sub&gt;∞&lt;/sub&gt;,exon (µA/cm²)</th>
<th>D (cm²·s&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>J (mol·(cm·s)&lt;sup&gt;−1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>570</td>
<td>20.82</td>
<td>7.34 × 10&lt;sup&gt;−7&lt;/sup&gt;</td>
<td>1.73 × 10&lt;sup&gt;−5&lt;/sup&gt;</td>
</tr>
<tr>
<td>0 g/L</td>
<td>580</td>
<td>20.28</td>
<td>7.21 × 10&lt;sup&gt;−7&lt;/sup&gt;</td>
<td>1.68 × 10&lt;sup&gt;−5&lt;/sup&gt;</td>
</tr>
<tr>
<td>3 g/L</td>
<td>1500</td>
<td>10.71</td>
<td>2.79 × 10&lt;sup&gt;−7&lt;/sup&gt;</td>
<td>8.88 × 10&lt;sup&gt;−5&lt;/sup&gt;</td>
</tr>
<tr>
<td>5 g/L</td>
<td>1620</td>
<td>6.15</td>
<td>2.58 × 10&lt;sup&gt;−7&lt;/sup&gt;</td>
<td>5.10 × 10&lt;sup&gt;−6&lt;/sup&gt;</td>
</tr>
<tr>
<td>7 g/L</td>
<td>1240</td>
<td>9.21</td>
<td>3.37 × 10&lt;sup&gt;−7&lt;/sup&gt;</td>
<td>7.64 × 10&lt;sup&gt;−6&lt;/sup&gt;</td>
</tr>
<tr>
<td>9 g/L</td>
<td>1140</td>
<td>14.18</td>
<td>3.67 × 10&lt;sup&gt;−7&lt;/sup&gt;</td>
<td>1.18 × 10&lt;sup&gt;−5&lt;/sup&gt;</td>
</tr>
</tbody>
</table>
3.3. Hydrogen adsorption

Figs. 11(a) and (b) show the structure of the single-layer WS\textsubscript{2} used in the calculation. A 2 \times 2 WS\textsubscript{2} supercell is adopted to investigate hydrogen adsorption to simplify the calculation. The five possible initial positions of hydrogen adsorption on the WS\textsubscript{2} surface are shown in Fig. 11(c), including the top site of W atoms (TW), bridge site of W atoms (BW), top site of S atoms (TS), bridge site of S atoms (BS), and hollow site of S atoms (HS). Table 2 lists the adsorption energies of hydrogen at different initial positions on the WS\textsubscript{2} surface. The adsorption energy of hydrogen at the BW position is the lowest of 1.488 eV, suggesting that the BW position is the most stable position for hydrogen adsorption on the WS\textsubscript{2} surface. Therefore, the hydrogen adsorption at the BW position is further analyzed.

The partial densities of states of WS\textsubscript{2} before and after hydrogen adsorption are shown in Fig. 12. The bandgap of WS\textsubscript{2} decreases from 1.95 eV to 1.20 eV after hydrogen adsorption, indicating that charge transfer occurs during adsorption, and electrons move from the valence band to conduction band. To clarify the electron trajectory, the partial densities of states of W and S atoms on the WS\textsubscript{2} surface before and after hydrogen adsorption are shown in Fig. 13. The 3p orbital of S coincides with the 1s orbital of H at 15 eV, 8 eV, and 4 eV after hydrogen adsorption, indicating orbital hybridization between S and H atoms. This may be caused by the formation of S—H bonds from the chemical reaction between S and H atoms.

Fig. 14 shows the charge density difference of WS\textsubscript{2} before and after hydrogen adsorption. The adsorbed H atom transfers 0.01 e charge to the adjacent S atom, and charge transfer between H and S atoms can be clearly observed from Fig. 14(b). This indicates that the H atom loses electrons during adsorption, thus forming S—H bonds with the S atom, which corresponds well to the conclusion in the partial density of states of WS\textsubscript{2}.

![Fig. 11. WS\textsubscript{2} structure: (a) Vertical view and (b) Side view; (c) Five possible initial positions for hydrogen adsorption.](image1)

![Fig. 12. Partial densities of states of WS\textsubscript{2} before and after hydrogen adsorption: (a) Hydrogen, (b) WS\textsubscript{2} before adsorption, and (c) WS\textsubscript{2} after adsorption.](image2)

<table>
<thead>
<tr>
<th>Adsorption position</th>
<th>Adsorption energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS</td>
<td>1.496</td>
</tr>
<tr>
<td>TW</td>
<td>1.985</td>
</tr>
<tr>
<td>BS</td>
<td>1.491</td>
</tr>
<tr>
<td>BW</td>
<td>1.488</td>
</tr>
<tr>
<td>HS</td>
<td>1.489</td>
</tr>
</tbody>
</table>
3.4. Mechanical properties and fracture morphology

The stress-strain curves of coated specimens with different WS$_2$ concentrations before and after hydrogen charging are shown in Fig. 15, and the mechanical properties are presented in Table 3. The invasion of hydrogen leads to the occurrence of HE, and the coated specimens deposited with different WS$_2$ concentrations exhibit different resistance to HE. The RA$\text{loss}$ values of the substrate and five groups of coated specimens are 66.2 %, 68.1 %, 73.9 %, 80.4 %, 77.1 % and 70.4 %, respectively. With increasing WS$_2$ concentration, the resistance to HE increases and then decreases, and the coated specimen deposited at 5 g/L shows the best resistance to HE.

As shown in Fig. 16, the fracture of coated specimens before hydrogen charging are dominated by dimple morphology, exhibiting ductile fracture caused by micro-void coalescence. In contrast, the fracture of coated specimens after hydrogen charging show obvious brittle characteristics, indicating HE occurs. Fig. 17 shows that the fracture of coated specimens after hydrogen charging has different fracture characteristics. Cleavage facets with a large area are observed from both the substrate and Ni-coated specimen, which indicates that the serve hydrogen-induced brittle fracture has occurred. When the WS$_2$ concentration increases from 0 g/L to 5 g/L, obvious dimples are observed from the fracture surface, suggesting that the fracture mode changes from cleavage to a combination of cleavage and micro-void coalescence. However, when the WS$_2$ concentration increases to 9 g/L, the fracture surface gradually restores the brittle fracture morphology dominated by cleavage facets. The results indicates that the coated specimens exhibit the resistance to HE, which reduces the hydrogen-induced plasticity loss. In addition, with increasing WS$_2$ concentration, the plasticity of specimens increases and then decreases in line with the SSRT test.

4. Discussion

The electrochemical hydrogen permeation test discloses that the composite coatings doped with WS$_2$ have lower D and J than the
substrate, indicating that WS$_2$ enhances the barrier effect against hydrogen permeation. However, it is not a simple positive correlation between the WS$_2$ concentration and resistance to hydrogen permeation. The resistance to hydrogen permeation increases first and then decreases with WS$_2$ concentration, and the best resistance is observed for 5 g/L. Although WS$_2$ can strengthen the barrier effects, the WS$_2$ concentration has an obvious effect on the resistance to hydrogen permeation. Therefore, it is necessary to explore the associated mechanism.

Based on the hydrogen adsorption simulation, it can be found that hydrogen atoms can form S–H bonds with S atoms on the WS$_2$ surface during permeation, meaning that the doping of WS$_2$ provides more

Fig. 15. Stress-strain curves: (a) 0 g/L, (b) 3 g/L, (c) 5 g/L, (d) 7 g/L, and (e) 9 g/L. 
hydrogen trapping sites to against the hydrogen permeation. In addition, existing studies [35,36] have shown that grain boundary of Ni can also play the role of hydrogen trap to capture the hydrogen atoms entering the coating. It can be inferred that the change of WS$_2$ distribution and Ni layer characteristics caused by WS$_2$ concentrations is likely the main reason for the change of the resistance to hydrogen permeation. Hence, the correlation among the WS$_2$ concentration, microstructure, and resistance to hydrogen permeation is analyzed in conjunction with the surface morphology characterization results in Section 3.1 and the hydrogen permeation tests results in Section 3.2, and the hydrogen permeation behavior for different WS$_2$ concentrations is further discussed. As shown in Fig. 18 (a), the pure Ni coating has poor uniformity and flatness due to different internal grain sizes and low compactness. The loose structure and pores provide a large number of hydrogen diffusion channels. As the WS$_2$ concentration increases to 3 g/L (Fig. 18 (b)), the uniformity and compactness of the Ni layer improve. The dense Ni layer resists rapid permeation of hydrogen, and the WS$_2$ deposited

**Table 3**

<table>
<thead>
<tr>
<th>Specimen</th>
<th>UTS (MPa)</th>
<th>El (%)</th>
<th>RA (%)</th>
<th>RA$_{nom}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>744</td>
<td>29.6</td>
<td>37.9</td>
<td>0.662</td>
</tr>
<tr>
<td>Substrate(H)</td>
<td>711</td>
<td>21.2</td>
<td>25.1</td>
<td>0.671</td>
</tr>
<tr>
<td>0 g/L</td>
<td>737</td>
<td>29.7</td>
<td>36.7</td>
<td>0.739</td>
</tr>
<tr>
<td>0 g/L(H)</td>
<td>715</td>
<td>21.6</td>
<td>24.6</td>
<td>0.804</td>
</tr>
<tr>
<td>3 g/L</td>
<td>751</td>
<td>29.1</td>
<td>38.3</td>
<td>0.739</td>
</tr>
<tr>
<td>3 g/L(H)</td>
<td>724</td>
<td>23.6</td>
<td>28.3</td>
<td>0.741</td>
</tr>
<tr>
<td>5 g/L</td>
<td>745</td>
<td>30.2</td>
<td>37.2</td>
<td>0.741</td>
</tr>
<tr>
<td>5 g/L(H)</td>
<td>717</td>
<td>27.5</td>
<td>29.9</td>
<td>0.804</td>
</tr>
<tr>
<td>7 g/L</td>
<td>745</td>
<td>29.3</td>
<td>37.1</td>
<td>0.771</td>
</tr>
<tr>
<td>7 g/L(H)</td>
<td>714</td>
<td>24.1</td>
<td>28.6</td>
<td>0.741</td>
</tr>
<tr>
<td>9 g/L</td>
<td>737</td>
<td>27.8</td>
<td>38.5</td>
<td>0.704</td>
</tr>
<tr>
<td>9 g/L(H)</td>
<td>716</td>
<td>21.8</td>
<td>27.1</td>
<td>0.704</td>
</tr>
</tbody>
</table>

**Fig. 16.** SEM micrographs of the uncharged specimens: (a) Substrate, (b) 0 g/L, (c) 3 g/L, (d) 5 g/L, (e) 7 g/L, and (f) 9 g/L.

**Fig. 17.** SEM micrographs of the hydrogen-charged specimens: (a) Substrate, (b) 0 g/L, (c) 3 g/L, (d) 5 g/L, (e) 7 g/L, and (f) 9 g/L.
inside the coating extends the hydrogen diffusion paths and provides hydrogen trapping sites to slow hydrogen diffusion and permeation. For the WS$_2$ concentration of 5 g/L (Fig. 18(c)), the grain size and structure of the Ni layer are further refined and densified, and the distribution of WS$_2$ is more uniform. The increase in the number of grain boundaries in the Ni layer and improved uniformity of WS$_2$ further extend the hydrogen diffusion path. Furthermore, more hydrogen traps are formed at the grain boundaries and WS$_2$ deposition sites. Ultimately, the $D$ and $J$ values decrease. However, an obvious accumulation of WS$_2$ is observed for 7 g/L (Fig. 18(d)) revealing disrupted uniformity. The stacking structure of WS$_2$ shortens the hydrogen diffusion path and decreases the hydrogen adsorption sites, leading to deteriorated resistance to hydrogen permeation. For the WS$_2$ concentration of 9 g/L (Fig. 18(e)), the grains in the Ni layer coarsen, and serious agglomeration of WS$_2$ occurs. The decrease in the number of grain boundaries caused by the coarsening of Ni shortens the hydrogen diffusion paths, and the barrier and trapping effects of WS$_2$ weaken due to severe agglomeration, giving rise to deteriorated resistance to hydrogen permeation.

The SSRT test and fracture analysis indicate that the coated specimens deposited with different WS$_2$ concentrations have different HE resistances. With increasing WS$_2$ concentration, the sensitivity to HE decreases and then increases. The lowest sensitivity to HE is achieved for a concentration of 5 g/L in line with the hydrogen permeation test. It can be inferred that the resistance to hydrogen permeation affects the resistance to HE. By using a WS$_2$ concentration at 5 g/L, excellent resistance to hydrogen permeation and HE is accomplished.

5. Conclusion

WS$_2$-Ni composite coatings with different WS$_2$ concentrations are prepared on X70 pipeline steel by electrodeposition. The effects of WS$_2$ concentrations on the microstructural morphology, resistance to hydrogen permeation and resistance to HE of WS$_2$-Ni composite coatings are investigated by microstructural characterization, electrochemical hydrogen permeation test, hydrogen adsorption simulation, SSRT test, and fracture analysis. Furthermore, the relationship of the WS$_2$ concentration, hydrogen permeation, and hydrogen protection is determined. The main conclusions are shown in the following:

1. With increasing WS$_2$ concentrations, the distribution of WS$_2$ in the composite coatings change from sparse, uniform, local agglomeration to severe agglomeration, and the grain size of the Ni layer decreases and then increases.

2. With increasing WS$_2$ deposition concentration, the resistance to hydrogen permeation increases initially and then decreases, with the best resistance for 5 g/L. The $D$ and $J$ values decrease to $2.58 \times 10^{-7}$ cm$^2$ s$^{-1}$ and $5.10 \times 10^{-6}$ mol/(cm$^2$ s), which are 3 times and 3.5 times less than those of the uncoated substrate, respectively.

3. The resistance to hydrogen permeation of the WS$_2$-Ni composite coatings depends on the microstructure and morphology and is closely related to the adsorption sites and diffusion paths of hydrogen in the coatings.

4. A similar influence of the WS$_2$ concentration is observed for the HE resistance, indicating improved HE resistance by resisting hydrogen permeation.
CRediT authorship contribution statement

Chilou Zhou: Writing – review & editing, Supervision, Resources, Funding acquisition, Conceptualization. Pengzhi Dai: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. Hao Wu: Writing – review & editing, Supervision, Project administration, Methodology, Conceptualization. Minglei Xie: Software, Methodology, Formal analysis. Jinxin Xue: Writing – original draft, Methodology, Investigation, Data curation. Yan Huang: Visualization, Software. Paul K. Chu: Writing – review & editing, Methodology, Funding acquisition.

Declaration of competing interest

The authors declare no conflict of interest.

Data availability

Data will be made available on request.

Acknowledgments

This research was jointly supported by the National Natural Science Foundation of China (Nos. 51705157 and 52075183), Guangdong Basic and Applied Basic Research Foundation (No.2022A151010692), Key-Area Research and Development program of Guangdong Province (No.2020B0404020004), National Foreign Expert Program (No. G20221630051L), City University of Hong Kong Strategic Research Grant (SRG 700505), and City University of Hong Kong Donation Research Grants (DON-RMG 9229021 and 9220061).

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