Study of the effect of nickel on toughness and hydrogen embrittlement resistance of X80 pipeline steel

Xiao Xing¹, Gonglin Deng¹, Chao Yang², Jian Guo Liu³, Gan Cui¹, Zili Li¹, and Yi Zhang¹

¹China University of Petroleum Huadong
²no affiliation
³China University of Petroleum Huadong - Qingdao Campus

November 2, 2022

Abstract

Experimental tests and molecular dynamics simulations were applied to investigate the mechanism of Ni concentration on the toughness and hydrogen embrittlement resistance of X80 steel. The tensile toughness, impact toughness, and hydrogen embrittlement resistance of X80 steel increase when Ni < 1%, followed by decreases when Ni > 1%. Especially, when the Ni concentration exceeds 3%, the hydrogen embrittlement resistance of the X80 steel is lower than that of the Ni-free specimen. The relationships between free surface energy, stacking fault energy, and unilateral passivation crack growth with Ni concentration were investigated by molecular dynamics simulations. The results prove that the increase of Ni concentration can simultaneously reduce the free surface energy and stacking fault energy of Fe-Ni alloys. And Ni atoms have a more significant effect on the reduction of stacking fault energy, so that the system releases energy through plastic deformation and inhibits the generation of cracks. However, as the Ni concentration exceeds 1%, martensite and carbides begin to form on the grain boundaries. The toughness and hydrogen embrittlement resistance of X80 steel decrease with the Ni concentration.
Experimental tests and molecular dynamics simulations were applied to investigate the mechanism of Ni concentration on the toughness and hydrogen embrittlement resistance of X80 steel. A slow strain rate test (SSRT) was carried out in the air and under electrochemical hydrogen charging conditions. The results verify that the threshold of toughness enhancement of X80 steel by Ni is 1%. The tensile toughness, impact toughness, and hydrogen embrittlement resistance of X80 steel increase when Ni < 1%, followed by decreases when Ni > 1%. Especially, when the Ni concentration exceeds 3%, the hydrogen embrittlement resistance of the X80 steel is lower than that of the Ni-free specimen. The relationships between free surface energy, stacking fault energy, and unilateral passivation crack growth with Ni concentration were investigated by molecular dynamics simulations. The results prove that the increase of Ni concentration can simultaneously reduce the free surface energy and stacking fault energy of Fe-Ni alloys. And Ni atoms have a more significant effect on the reduction of stacking fault energy, so that the system releases energy through plastic deformation and inhibits the generation of cracks. However, as the Ni concentration exceeds 1%, martensite and carbides begin to form on the grain boundaries. Martensite is a hard and brittle phase with a strong sensitivity to hydrogen embrittlement. Also, the carbides segregate at the grain boundaries and promote intergranular fracture. Therefore, when the Ni concentration is higher than 1%, the toughness and hydrogen embrittlement resistance of X80 steel decrease with the Ni concentration.

Keywords: X80 steel, Fe-Ni alloy, hydrogen embrittlement resistance, toughness

1. Introduction

Pipeline steel (X series pipes) has many advantages such as stability, safety, economy, and environmental protection in transporting oil and natural gas. According to the latest report, the total length of the global transmission pipeline is 2034065.0 km (year of initiation to 2023). The trend of development of oil and gas long-distance pipelines is of large diameter and high pressure. To meet this requirement, the application of high-strength steel is gradually increased [1]. Currently, the most widely used is X80 pipeline steel [2,3]. Also, new progress has been made in the research of high-strength X100 and X120 steels. However, the ductility and fracture toughness of high-strength steel (X80) are significantly reduced compared to X52 and X65 steel, making fracture accidents more likely to occur [4,5]. Improving its ductility while ensuring the strength of pipeline steel has become a technical issue in the energy transportation industry.

In addition, as the most promising secondary energy source, ensuring the efficient and stable delivery of hydrogen is also an obstacle to the development of hydrogen energy [6]. Using the existing natural gas pipeline network for hydrogen doping transmission can achieve energy storage, power peak shaving, and valley filling. Additionally, avoiding the high construction cost of new hydrogen pipelines [7,8], while studies have shown that the cost of hydrogen pipelines is 68% higher than that of natural gas pipelines [9]. However, due to the strong permeability of hydrogen, hydrogen atoms can penetrate the pipe and cause hydrogen embrittlement. The higher the steel grade, the weaker the resistance to hydrogen embrittlement [10,11]. Nanninga et al. [11,12] tested the tensile properties of X52, X60, and X100 pipeline steels in the air and hydrogen gas environment. The results show that the elongation of the specimen in hydrogen gas can be reduced from 20% to 50% when compared with results in the air for smooth specimens. For notched specimens, the reduction in elongation could be more prominent, and the reduction could reach 80% relative to the elongation tested in the air [13]. Hardie [14] studied X80 steel and found that the elongation was 19% without hydrogen, and when the cathodic charging current density was 0.44 mA/cm², the elongation decreased to 4%.

For the above reasons, many studies have been carried out to improve the properties of pipeline steels in hydrogen environments, most of which are developed by adding various alloying elements to develop tougher steels [15–19]. Among these elements, Ni is considered to be an effective element for enhancing the toughness of low-alloyed high-strength steels [2,7,8]. The Ni exists in the form of solid solution in the ferrite matrix and does not form second phase particles, indicating that the strength of Ni-added steel can be improved by solid solution strengthening [22]. Also, Ni can promote the transformation of austenite into pearlite during the
cooling process of the steel [23]. Chawlan [24] et al. studied Fe-Mo alloys with different concentrations of Ni and found that the elongation of the alloy increased from 1.5% without Ni to 3.5% when the Ni content was 2wt%. Also, the porosity and grain size of Fe-Mo alloys decreased after adding Ni element. Lan Yin, S et al. [25] studied the effect of pores on the plasticity of iron-based metallurgical materials. They used Fe-Cu as the matrix and found that the elongation of the alloy was also improved from 2.5% to 4% by adding Ni. The microscopic study also found that the addition of Ni reduced the pores in the alloy. However, Ryoo et al. [26] studied the effect of Ni (8.3~12wt.%) on the tensile properties of 304 stainless steel and found that the tensile strength of the alloy decreased with the increase of Ni content at room temperature, and the yield strength approximated constant. Liu et al. [27] found that the Fe-Ni alloy’s yield strength and maximum tensile strength increased significantly with the Ni concentration, while the elongation also increased with the increase of Ni when the Ni mass fraction was less than 0.6%. As the Ni fraction is greater than 6%, the elongation of the alloy decreases with the increase of Ni. Chen et al. [28] applied molecular dynamics simulation and obtained that when the Ni concentration increased from 0.5 to 6.0 at%, the Young’s modulus and ultimate stress of Fe-Ni alloy nanowires gradually increased. When the Ni concentration is further increased to 8.0 at%, the Young’s modulus and ultimate stress decrease with the increase of Ni concentration. Pogorelko et al. [29] prove that nickel is an inclusion in the iron matrix, which is easy to cause fracture and reduce the tensile strength of Fe-Ni alloys. There is no consensus on the influence of Ni on the property of Fe-based alloys. Whether Ni can reduce the hydrogen embrittlement susceptibility of X80 steel remains to be studied. Therefore, this paper studies the influence of Ni concentration on the mechanical properties and hydrogen embrittlement resistance of X80 steel through slow tensile experiments and Charpy impact experiments. The Ni concentration that optimizes the performance of the X80 pipeline is tested. This research provides a reference to determine the proper concentration of Ni in the pipeline steel to achieve great performance in hydrogen embrittlement resistance. Moreover, this study is beneficial for understanding the modification mechanism of Ni in other structural materials.

2. Experimental Methodology

During the casting, the total content of Ni and Fe is 97.215%, and the weight ratio of Ni is 0%, 1%, 2%, 3%, and 5%. The smelting composition is determined according to the API Spec 5l-2012, specification for pipeline steel pipe hot-rolled wide steel strip for oil and gas pipelines, as shown in Table 1. X80 steel is smelted in a vacuum induction furnace [25] and cast into 5kg ingots.

Table 1 Chemical smelting composition of X80 steel (mass fraction, %)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Nb</th>
<th>Ti</th>
<th>Al</th>
<th>Cu</th>
<th>Ni</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05</td>
<td>0.28</td>
<td>1.83</td>
<td>0.011</td>
<td>0.003</td>
<td>0.03</td>
<td>0.22</td>
<td>0.05</td>
<td>0.061</td>
<td>0.02</td>
<td>0.03</td>
<td>0.2</td>
<td>0</td>
<td>Bal.</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>0.28</td>
<td>1.83</td>
<td>0.011</td>
<td>0.003</td>
<td>0.03</td>
<td>0.22</td>
<td>0.05</td>
<td>0.061</td>
<td>0.02</td>
<td>0.03</td>
<td>0.2</td>
<td>1</td>
<td>Bal.</td>
</tr>
<tr>
<td>3</td>
<td>0.05</td>
<td>0.28</td>
<td>1.83</td>
<td>0.011</td>
<td>0.003</td>
<td>0.03</td>
<td>0.22</td>
<td>0.05</td>
<td>0.061</td>
<td>0.02</td>
<td>0.03</td>
<td>0.2</td>
<td>2</td>
<td>Bal.</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
<td>0.28</td>
<td>1.83</td>
<td>0.011</td>
<td>0.003</td>
<td>0.03</td>
<td>0.22</td>
<td>0.05</td>
<td>0.061</td>
<td>0.02</td>
<td>0.03</td>
<td>0.2</td>
<td>3</td>
<td>Bal.</td>
</tr>
<tr>
<td>5</td>
<td>0.05</td>
<td>0.28</td>
<td>1.83</td>
<td>0.011</td>
<td>0.003</td>
<td>0.03</td>
<td>0.22</td>
<td>0.05</td>
<td>0.061</td>
<td>0.02</td>
<td>0.03</td>
<td>0.2</td>
<td>5</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Initially, the raw material is desulphurized and slag skimmed at 1450-1500 °C. The Ladle Furnace (LF) refining and continuous casting process are subsequently applied to the steel. Afterward, cleaning, heating, and rolling process are employed. The details of the cooling rate, heating rate, and rolling temperature have been shown in Table 2.

Table 2 Refining process of steel

3
The specimen geometry is shown in Fig. 1 (a). At room temperature, slow strain rate test (SSRT) specimens were cut along the rolling direction of the material to ensure that the stress loading direction was perpendicular to the direction of the fracture surface found in the field. The samples are processed according to the standard. Before testing, the specimens were ground to 2000 grit, then numbered, and sealed with silicone at both ends. Grinding direction should be consistent with the direction of tensile stress to ensure that no surface cracks will occur during loading. Then, rinse the specimen with acetone, deionized water, and alcohol to remove debris from the test section. After cold air drying, the specimens were placed in a desiccator for 24 hours. The SSRT is carried out under air or dynamic electrochemical hydrogen charging conditions. Dynamic electrochemical hydrogen charging is performed simultaneously with hydrogen charging and stretching, and the hydrogen charging time is from the beginning of stretching to the fracture of the specimen. The sample is placed in a sealed box so that the exposed middle slender part of the sample is in contact with the electrolyte medium, and the rest of the sample is sealed with silica gel. The electrolyte adopts 0.5 mol/L H₂SO₄ and 0.2 g/L thiourea solution. The sample was connected to the cathode, and the platinum sheet was used as the anode. The sample was electrochemically charged with hydrogen by the galvanostatic method. The hydrogen charging current density was 50 mA/cm² and 20 mA/cm², respectively. The hydrogen charging box is shown in Fig. 1 (b). A vertical tank is used to keep the hydrogen-charging box under a constant temperature of 20 °C. The tensile speed is 0.002 mm/min, corresponding to a strain rate of about 1×10⁻⁶ /s. After the test, all specimens shall be ultrasonically cleaned with a rust remover. Subsequently, the samples were cleaned with alcohol and dried with cold air. The elongation of the sample will be measured. The fracture morphology of the samples was observed by scanning electron microscope (SEM).
3. Results and discussion

3.1 The effect of Ni on the toughness of X80 steel

The metallographic images of X80 steel at five Ni concentrations are shown in Fig. 2 below. The primary microstructure of all X80 steel samples is polygonal ferrite (F) and a small amount of granular bainite (B). The proportion of ferrite in the steel decreases as the Ni concentration increases from 0% to 1%. Simultaneously, the relative content of granular bainite increases, and austenite appears. However, with the further increase of Ni content, the precipitation phase of the steel sample gradually turns from white to black, the austenite content decreases, and carbide (Fe₃C) and martensite (M) gradually form at the grain boundary.
$c_{\text{Ni}} = 2\%$

M+$\text{Fe}_3\text{C}$

$25\mu\text{m}$

$\overbrace{\text{ }}$

$c_{\text{Ni}} = 3\%$

M+$\text{Fe}_3\text{C}$

$25\mu\text{m}$
Fig. 2. (a) Metallographic structures of steel samples with different Ni concentrations; (b) colored metallographic structures of steel samples with different Ni concentrations.
The stress-strain curves of the steel specimen with different Ni concentrations in air at room temperature are shown in Fig. 3 (a). The mechanical properties are listed in Table 3. The strain-stress curve can be divided into the elastic deformation and plastic deformation stages. The curves of the elastic deformation stage coincide, indicating that Ni has little effect on the elastic modulus of X80 steel. Compared with the specimen without Ni, the toughness of the specimen with Ni (which can be expressed as the area enclosed by the curve and the X coordinate axis) increases, indicating that the Ni element enhances the toughness of the X80 steel. The toughness of X80 steel reaches the maximum when it contains 1% Ni, while its tensile strength is the smallest. Afterward, with the increase of Ni concentration, the toughness gradually decreases, and the tensile strength gradually increases. Fig. 3 (b) shows the impact energy of steel specimens with different Ni contents. The results show that the Ni composition has a significant effect on the impact energy. The impact energy increases initially, then decreases with the increase of Ni concentration. When the Ni concentration is 1%, the steel has the strongest impact toughness, and the impact energy reaches 35.3 J, which is 60.5% higher than that of Ni-free steel. When the Ni concentration increases to 2%, the impact energy is 33.7 J, which is 53.2% higher than that of the Ni-free sample. When the Ni content reaches 3% and 5%, the impact energy only increases by 19.5% and 9.1% compared with the Ni-free sample, respectively. It demonstrates that the impact toughness is not positively correlated with the Ni concentration. There is a threshold of the Ni content on toughening effect on X80 steel. In this study, when a 1% weight ratio Ni is introduced, the impact toughness reaches the maximum.

The influence of Ni on the tensile strength, tensile toughness, and impact toughness of X80 steel can be explained by the microstructure. When the Ni concentration is zero, the steel is composed of ferrite and a small amount of bainite. When the Ni content increases to 1%, Ni promotes the formation of retained austenite (A). It has been reported that austenite can hinder the nucleation and propagation of cracks [30]. Thus, steel yield strength is reduced, and the toughness is significantly increased. When the Ni concentration is further increased, Ni promotes the transformation of austenite to martensite. Because martensite is a hard and brittle structure, the tensile strength of the steel increases with the increase of the martensite. While the tensile toughness and Impact toughness decrease. When the Ni concentration is 1%, the austenite content in the steel is the highest, and the martensite has not yet been formed, so the tensile and impact toughness of the steel reaches the maximum, and the tensile strength reaches the minimum. The fracture
morphology in the air was observed by scanning electron microscope (SEM) (Fig. 4). The fracture cross-section at 100 times microscope elucidates that the fracture mechanism of the five alloys is a ductile-brittle mixed fracture mode composed of micropore aggregation fracture and quasi-cleavage fracture. The fracture morphology of the sample without Ni shows that the cleavage fracture area is large, the number of dimples is little, and the plasticity of the specimen is poor. The tensile fracture of the samples containing 1% and 2% Ni concentrations have fewer pores and cleavage surfaces, and more dimples on the fracture surface, so they have better plasticity. The high-resolution results also verify that the fracture surface of the Ni-free specimen is relatively flat, showing a river pattern. Both $c_{\text{Ni}} = 1\%$ and $c_{\text{Ni}} = 2\%$ are ductile fractures, showing dimple-like fracture morphology. Among them, the $c_{\text{Ni}} = 1\%$ fracture surface has the largest and deepest dimples, indicating the best toughness. Subsequently, the Ni concentration gradually increases, but the dimples gradually become shallower and smaller, indicating that the toughness gradually decreases. The fracture surfaces of $c_{\text{Ni}} = 3\%$ and $c_{\text{Ni}} = 5\%$ have both dimples and dissociation planes, indicating that they are quasi-cleavage fractures. With the increase of Ni, the fractured style of X80 steel transits from brittle to ductile, and then back to brittle. When the Ni content is low, it can promote the formation of austenite and enhance the toughness of X80 steel. With the increase of Ni, the impurity atoms (P, Sn, Si, S, etc.) segregate at the grain boundary, and the brittle phase precipitates at the grain boundary \[31,32\]. Thus, the X80 steel undergoes quasi-cleavage brittle fracture.
$c_{\text{Ni}} = 3\%$

$10\mu m$ JEOL 11/16/2021
x2,000 15.0kV LED SEM WD 17.9mm 13:03:03

$100\mu m$ JEOL 11/16/2021
x100 15.0kV LED SEM WD 17.9mm 12:47:46

$c_{\text{Ni}} = 5\%$
SSRT experiments in the air have proved that Ni atoms at low concentrations have a toughening effect on steel. When the Ni concentration increases, it leads to the rapid precipitation of martensite, which is a brittle phase. However, compared with the specimen free of Ni, the toughness of the specimen with Ni content higher than 2% is still better. In addition to the effect of Ni on the phase change, there should be other mechanisms that affect the modification effect of Ni on X80 steel, and Ni might have a significant effect on the stacking fault energy and surface energy of the iron. Therefore, the change of stacking fault energy and surface energy of body center cubic (BCC) iron affected by Ni concentration is studied with the molecular dynamics method.

All simulations were carried out using LAMMPS [33]. Two body center cubic models are built to calculate the free surface energy [34] with crystallographic fracture planes (110) and (112), respectively, which are perpendicular to the z dimension. The details of both systems are indicated in Table 4. The iron atoms along the fracture plane are substituted by Ni atoms, as shown in Fig. 5 (a). As the model is separated along the fracture plane, the energy difference of intact and separated states to the fracture surface area yields the free surface energy, \( \gamma_s \) [35]. The expression of \( \gamma_s \) is shown as follows:

\[
\gamma_s = \frac{E_s - E_0}{2A} \quad (1)
\]

Where \( E_s \) is the total energy of the separated system, \( E_0 \) is the energy of the intact system, and \( A \) is the area of the free surface. The results are shown in Fig. 6.

**Table 4 The details of two simulated systems in calculating free surface energy**

<table>
<thead>
<tr>
<th>Fracture Plane</th>
<th>Dimensions(Å)</th>
<th>Number of atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110)</td>
<td>36.4Å<em>17.2Å</em>60.7Å</td>
<td>3240</td>
</tr>
<tr>
<td>(112)</td>
<td>35Å<em>16.2Å</em>59.5Å</td>
<td>2880</td>
</tr>
</tbody>
</table>
Fig. 5. (a) The model to calculate the free surface energy. The iron atoms are indicated in red and blue ones are Ni atoms; (b) The model to calculate stacking fault energy by a sliding system

Hosted file


Fig. 6. Free surface energy is in a function of atomic Ni concentration on \{112\} and \{110\} planes.

The simulated results verify that free surface energy decreases slightly with the increase of Ni content. The reduction is negligible since the variation scale of free surface energy is limited to 5%. The cleavage stress intensity, $K_{Ic}$, is positively related to the $\gamma_s$, which indicates that Ni has little effect on the cleavage damage generation in Fe-based alloy. The free surface energy of the \{112\} plane is much larger than the \{110\} plane, because the \{110\} plane is more close-packed than the \{112\}. Hence, the distance between the two \{110\} planes is much larger, resulting in smaller bonding energy.

At room temperature, the primary slipping system of dislocations in a-Fe is $<111>$\{112\} (slip direction)\{slip plane\} [36]. The dislocation emission stress intensity is positively related to the stacking fault energy, $\gamma_{us}$. The $\gamma_{us}$ is a ratio of energy difference of intact and slipping states to the cross-sectional area, which measures plastic deformation. To calculate the stacking fault energy, an $\alpha$-iron single crystal model is constructed, and the slip system of the dislocation is calculated in $<111>$\{112\} slipping system. The orientations of the model are: x-[110], y-[111], z-[112]. The dimensions are 4.20435 nm, 12.1369 nm, and 23.7834 nm, respectively. The iron atoms on the slip plane were randomly replaced by Ni atoms with different

(a) (b)
concentrations, as shown in Fig. 5 (b). The ratio of the energy difference between the intact state and the slip state to the cross-sectional area is the stacking fault energy.

The correlation between generalized stacking fault energy (GSFE) and slipping displacement is shown in Fig. 7 (a). The unstable stacking fault energy (USFE) is the peak value of the GSFE at a specific Ni concentration, which is shown in Fig. 7 (b). As the atomic concentration of Ni increases, the USFE of the system decreases. The reduction of USFE indicates that Ni atoms would decrease the energy needed for dislocation emission in Fe-based alloy. Ni atoms enhance the plastic deformation and enhance the fracture toughness of single crystal Fe. The way Ni affects the stacking fault energy makes ferrite more prone to plastic deformation at room temperatures [37]. Therefore, as the Ni concentration increases, less energy is required for dislocation slip. As the atomic concentration approximates unity, the slipping plane is completely Ni plane, and the USFE value approximates the value in the pure Ni system. The USFE in the pure Fe system approximates 900 mJ/m² [38], while the USFE in the pure Ni system approximates 500 mJ/m² [39]. The USFE could be decreased up to 55% by introducing Ni atoms into an iron alloy.

To simulate the transgranular cracking in the steel, an initial crack is located in the middle of the z-axis. The total length of the initial crack is 30 Å, and the width of the opening mouth is 10 Å.

The stress value of iron atoms in the stress concentration area at the crack tip is calculated, and the stress-strain curve in the stress concentration area is obtained, as shown in Fig. 8. In the strain range of 0-0.04, the model is in the linear elastic stage, and the yield strengths of models are all lower than those of the pure iron model without Ni, indicating that Ni atoms can promote the plastic deformation of iron-based alloys. With the increase in Ni concentration, the toughness of the iron-based alloy is stronger.

In Fig. 8, the dislocation emits at a strain of 4.2% as no Ni exists in the system. The strains of dislocation emission in 1% and 5% Ni models are 4.1% and 3.7%, respectively. The crack resharpening strain decreases from 5.2% to 4.8% as the Ni concentration increases from 0 to 5%. The Ni atoms decrease the USFE in Fe-Ni alloy, thus, enhancing the dislocation emission. Also, Ni atoms decrease the free surface energy and facilitate the dormant crack resharpening. As shown in Fig. 9, as the Ni concentration increases, the dormant crack is prone to emit dislocation at a smaller strain and propagates at a smaller strain. However, at \( c_{\text{Ni}}=0.05 \), the
resharpening crack is arrested in the subsequent load. As the strain loading increases, lots of dislocations emit from the crack tip. The increased strain energy is typically cost by plastic deformation. The crack remains dormant as the strain increases to 7.7% of 5% Ni concentration, while the completely cracking happens in the low Ni system at a much smaller strain of 6%. The transgranular crack transits from quasi-brittle to ductile as Ni increases.
(a) $c_{Ni} = 0 \, \varepsilon = 4.2\% \, \varepsilon = 5.2\% \, \varepsilon = 6\%$
(b) $c_{\text{Ni}}=0.01$ $\varepsilon=4.1\%$ $\varepsilon=4.9\%$ $\varepsilon=6.1\%$
Fig. 9. Schematic of Y-Z plane versus the strain loading on Y dimension, as the Ni atomic concentration changes from 0 to 5%. (a) The crack resharpening process as $c_{\text{Ni}}$ equals to 0, the green indicates BCC structure, and red indicates unknown structure; (b) the crack resharpening process as $c_{\text{Ni}}$ equals to 0.01; (c) the crack resharpening process as $c_{\text{Ni}}$ equals to 0.05.
3.2 The influence of Ni on the resistance of hydrogen embrittlement of X80 steel

Comparing the fracture strains in Fig. 10 (a) and Fig. 10 (b), it is found that when the hydrogen charging current increases from 20 mA/cm$^2$ to 50 mA/cm$^2$, the time taken for complete fracture of X80 pipeline steel with $c_{\text{Ni}} = 0$, $c_{\text{Ni}} = 1\%$, and $c_{\text{Ni}} = 2\%$ is reduced by 7%, 25%, and 19%, respectively. It also verifies that the greater the hydrogen charging current, the stronger the hydrogen embrittlement effect. Under the two hydrogen charging currents, the influence of the Ni element on the toughness and strength of X80 steel is consistent. When $c_{\text{Ni}} = 1\%$, the toughness and tensile strength of X80 steel reach maximum. With the further increase of Ni concentration, the toughness and tensile strength gradually decrease. When the concentration of Ni exceeds 3%, the toughness, plasticity, and tensile strength drop below those of Ni-free specimens. Therefore, when the addition of Ni atoms is less than 2%, Ni atoms can increase the hydrogen embrittlement resistance of X80 steel. When the addition of Ni atoms is greater than 2%, Ni atoms will increase the hydrogen embrittlement sensitivity of X80 steel.

The hydrogen embrittlement susceptibility of a material is usually evaluated by the ratio of the material elongation loss before and after hydrogen charging, and the expression is:

$$\delta_{\text{sol}} = \frac{\delta_{\text{sol}}}{\delta_{\text{air}}}$$

Where $\delta_{\text{air}}$ is the elongation of material in air, $\delta_{\text{sol}}$ is the elongation under hydrogen charging condition. Typically, the value of $I_{\delta}$ is between 0 and 1, and the larger the value, the higher the hydrogen embrittlement susceptibility of the material. Generally, the strain rate should be lower than $10^{-3}$ s$^{-1}$ when evaluating the hydrogen embrittlement susceptibility of the material by the slow tensile test [40]. In the current study, the strain rate of $10^{-6}$ s$^{-1}$ was used to evaluate the hydrogen embrittlement susceptibility of the material.

The variation of hydrogen embrittlement susceptibility with Ni concentration under different hydrogen charging currents is shown in Fig. 11. With the increase of Ni concentration, the hydrogen embrittlement susceptibility of X80 steel decreased initially and then increased. Under different hydrogen charging currents, the hydrogen embrittlement susceptibility reaches the minimum when the Ni content is 1%. When the content of the Ni element is below 2%, the addition of Ni is beneficial in reducing the susceptibility of hydrogen embrittlement. When the content of Ni exceeds 3%, the increase of Ni will increase the susceptibility of the specimen to hydrogen embrittlement.

Fig. 11. Variation of hydrogen embrittlement sensitivity with Ni concentration under hydrogen charging current of 20 mA/cm$^2$ and 50 mA/cm$^2$. 
When the material is electrochemically charged with hydrogen, H can be compounded into H$_2$ at some defects or voids in the steel. When the hydrogen pressure is greater than the yield strength, the hydrogen blistering forms at the fracture surface. When the hydrogen pressure is greater than or equal to the atomic bonding force, the microcracks will appear. Both hydrogen blistering and hydrogen pressure cracking are irreversible damage, which can easily cause steel failure [41,42].

The images of hydrogen blistering and cracks on the surface with optical microscopes are shown in Fig. 12 and 13, under two hydrogen charging current densities. When the Ni concentration is equal to 0, there is serious hydrogen blistering on the sample surface. When the Ni concentration increases to 1%, the hydrogen blistering disappears. Under 20 mA/cm$^2$ hydrogen charging current, when the Ni concentration increases to 2%, hydrogen pressure cracks appear on the specimen surface. With the increase of Ni concentration to 3% and 5%, hydrogen blistering is observed on the sample surface. We observed the specimen surface under the hydrogen charging current of 50 mA/cm$^2$. When the Ni concentration increases to 2%, there is hydrogen blistering but no crack. As the Ni concentration increases to 3% and 5%, large cracks appear on the fracture surface. In conclusion, introducing 1% Ni into X80 steel can inhibit the generation of hydrogen blistering and hydrogen pressure crack. When the Ni concentration increases beyond 3%, the hydrogen blistering appears, also, the secondary cracks generate.
Fig. 12. Fracture morphology under hydrogen charging current of 20mA/cm²
During the dynamic electrochemical hydrogen charging tensile test, the fracture surface and tensile stress axis of pipeline steel are at an angle of nearly 45°, and there is no obvious necking phenomenon. In Fig. 14 (a), the SEM images of the cross-section of the sample under the hydrogen charging current of 20 mA/cm² at 100 magnification are shown. When the Ni content is at a low concentration, there is no crack on the surface. When the Ni concentration exceeds 3%, secondary cracks appear on the fracture surface. With the increase of Ni concentration, the number of secondary cracks increased, and the size of the cracks became larger.

In Fig. 14 (b), cross-section images of the sample under 20 mA/cm² hydrogen charging current at 2000 magnification are shown. There are rows of tearing edges on the $c_{Ni}=0$ fracture surface, and the quasi-cleavage planes are distributed in the rows of tearing edges. Between the cleavage edges, a special cleavage morphology, namely the "header" shape, appears in the middle of the plane. A large number of tearing edges appear at the plane boundary, which is due to the obvious plastic deformation at the grain boundary when the crack generates and propagates inside the grain. Although the steel with $c_{Ni}=1\%$ and $c_{Ni}=2\%$ become brittle due to hydrogen charging, the fracture type is still a dimpled fracture. However, the fracture morphology of dynamic hydrogen charging samples of $c_{Ni}=3\%$ and $c_{Ni}=5\%$ specimens showed obvious cleavage characteristics, and a large number of secondary cracks were detected. The introduction of hydrogen increases the number of microporous nucleation, resulting in a decrease in the plasticity of the material. Also, dislocations trap hydrogen atoms. With the increase of Ni concentration, the solid solution strengthening effect of Ni leads to phase change at the grain boundary. The brittle phase causes the aggregation of dislocations and hinders the movement of hydrogen atoms, so the cracks increase at the fracture surface. Therefore, with an increase of the Ni concentration beyond 3%, the toughness of the specimen will be significantly reduced.

Energy Dispersive Spectroscopy (EDS) surface scanning was performed on the fracture surfaces of the samples. The element distribution of the specimen when $c_{Ni}=5\%$ is shown in Fig. 15. The content of Ni and C is higher at the tearing edge, and less in the dimple and the dissociation surface. In order to confirm whether Ni and C are segregated at the tearing edge or grain boundary, further point scanning was carried out. EDS element point scanning was performed on the fracture surface of the 5% Ni specimen. The distribution of each element is shown in Fig. 16. Spectrum 1 is the element distribution on the grain boundary, and spectrum 

![Fracture morphology under hydrogen charging current of 50mA/cm²](image-url)
2 indicates the tearing edge. Spectrum 3 is the element distribution at the dimple, and spectrum 4 is the element content on the quasi-cleavage surface. The Ni concentrations on the fracture surface, grain boundary, and tearing edge are much larger than those at the dimple. The Ni segregates at the grain boundaries and facilitates carbide formation there. Also, the fracture of the specimen showed an intergranular feature, indicating that the segregation of carbides at the grain boundaries aggravated the hydrogen embrittlement at the grain boundaries. According to the metallographic diagram in Fig. 2, when the Ni element exceeds 1%, more martensite is formed at the grain boundary of the specimen, and the martensite is sensitive to hydrogen embrittlement. Even though the Ni could decrease the stacking fault energy and enhance dislocation emission in Fe-Ni alloy, it still enhances the segregation of hydrogen in grain boundaries. Therefore, there is a threshold of Ni concentration for the improvement of the hydrogen embrittlement resistance of X80 steel. As the Ni concentration exceeds the threshold, the hydrogen embrittlement resistance of the specimen is even lower than that of the Ni-free specimen.
$c_{\text{Ni}} = 2\%$

$\text{SEM} 12/16/2021$

$x2,000 15.0 \text{kV LED SEM WD 18.6mm 09:59:35$

$\text{x100 15.0 \text{kV LED SEM WD 18.4mm 10:04:54$

$c_{\text{Ni}} = 3\%$


$c_{\text{Ni}} = 3\%$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$

$\quad$
Fig. 14. SEM of fracture surface at 20mA/cm² hydrogen charging current, (a) 100×; (b) 2000×
Fig. 15. (a) EDS fracture surface element distribution diagram (surface scanning), blue indicates nickel element, purple indicates carbon element; (b) Ni distribution; (c) C distribution.

Fig. 16. EDS element map of $c_{\text{Ni}}=5\%$ X80 steel sample, the graphs correspond to the element analysis of points 1, 2, 3 and 4 in Fig. 14.
Conclusion

In this paper, the effect of Ni concentration on the toughness of X80 steel in air and hydrogen environment was studied by experimental tests and molecular dynamics simulation. The conclusions are as follows:

(1) When the Ni concentration is low, the microstructure of X80 steel is mainly ferrite, of BCC structure. Ni atoms can reduce the stacking fault energy and free surface energy of the ferrite. However, the reduction of Ni on stacking fault energy is more significant. Dislocation emission costs the strain energy increment, thereby inhibiting the crack propagation so that the toughness of the matrix is strengthened. However, with the increase of Ni concentration, martensite and carbide segregate at grain boundaries, which induces grain boundary hardening. Also, carbide on grain boundaries blocks dislocation slip, which improves the strength and hardness of the matrix. These two antagonistic mechanisms lead to the existence of a Ni concentration threshold for the toughening of X80 steel.

(2) The steel incorporated with 1% Ni atom possesses the highest impact toughness. When the Ni concentration is 2%, due to the precipitation of cementite, the grain boundary hardening phenomenon occurs, so the strength is also significantly enhanced compared with the Ni-free and 1% Ni specimen. When the concentration exceeds 2%, the cementite precipitates on the grain boundary. With a further increase of Ni, the proportion of martensite in the material increases significantly, inducing brittle intergranular fracture and quasi-dissociative fracture, and a significant decrease in toughness.

(3) When the hydrogen charging current is 20mA/cm$^2$, the tensile fracture morphology of X80 steel with Ni concentrations of 0, 2%, 3%, and 5% exhibits a quasi-cleavage feature. When the Ni concentration is 1%, the dimple fracture occurs. With the increase of Ni concentration, the fractured style transits from brittle to ductile, then back to brittle. When increasing the hydrogen charging current to 50 mA/cm$^2$, the fracture morphologies of all specimens became quasi-cleavage fractures, and when the Ni concentration was 5%, the secondary crack intergranular fracture was detected.

(4) Under dynamic hydrogen charging conditions, when the Ni concentration increased from 0 to 1%, the strength, toughness, plasticity, and hydrogen embrittlement resistance of X80 steel were enhanced due to the Ni effect on stacking fault energy reduction and austenite formation. Gradually, a further increase in Ni concentration decreases the strength, toughness, plasticity, and hydrogen embrittlement resistance. Especially, when the Ni concentration exceeds 3%, the hydrogen embrittlement resistance of the steel is lower than that of the Ni-free specimen. At this concentration, Ni atoms promote the formation of martensite and carbides on the grain boundary. Martensite and carbides enhance the hydrogen trapping effect of the grain boundary, thus promoting intergranular fracture. Therefore, introducing 1% Ni into the X80 steel achieves the best hydrogen embrittlement resistance.

Acknowledgement

The authors would like to acknowledge the financial support from the National Natural Science Foundation of China (52004323), Natural Science Foundation of Shandong Province (ZR2020ME094), Qingdao Postdoctoral Applicable Foundation (BY20170214), Natural Science Foundation of Shandong Province (ZR2019BEE006), PetroChina Innovation Foundation (Grant No. 2019D-5007-0505), Innovative Fellowships of the China University of Petroleum (East China) (18CX02175A), Fundamental Research Funds for the Central Universities (18CX05002A), Natural Science Foundation of Shandong Province (ZR2019MEE108), and the Fundamental Research Funds for the Central Universities (No. 18CX02078A).

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Reference