Effect of Heat Input on Microstructure and Corrosion Resistance of X80 Laser Welded Joints

Wei Zhao 1,2,*, Jia Wang 1,2, Zhen Li 1,2, Ning Guo 1,2 and Song Gao 1,2

Abstract: Using fiber laser welding technology, X80 pipeline steel welded joints with different welding heat inputs were obtained. Their microstructure, mechanical properties, and corrosion resistance (in NACEA solution saturated with hydrogen sulfide) were studied. Findings indicated that with the increase in heat input, the proportion of ferrite, strength, elongation, and corrosion resistance increased within a certain range and the sum of the proportion of martensite and bainite and hardness decreased. The heat input has a greater effect on the microstructure of weld metal (WM) and coarse-grained heat-affected zone (CGHAZ), while that of fine-grained heat-affected zone (FGHAZ) is basically unchanged. Obvious differences are also found in the corrosion resistance of different regions of the welded joints, among which FGHAZ has the strongest corrosion resistance, followed by WM and CGHAZ. The heat input mainly affects the microstructure type of the welded joint to affect the corrosion resistance. Therefore, we model the heat input as a function of \( R_{ct} \) and \( i_{corr} \) from this relationship. In addition, the corrosion products film produced by the long-term immersion of the welded joint in the saturated H\(_2\)S NACEA solution can hinder the development of corrosion and enhance the corrosion resistance to a certain extent.

Keywords: X80 pipeline steel; laser welding; heat input; H\(_2\)S corrosion

1. Introduction

The development of pipeline steel with high strength and toughness, benefiting from the increasing demand for oil and natural gas around the world, has been the focus of considerable attention. As one of the high-strength low-alloy steels, X80 pipeline steel has high strength and toughness and has been widely used in pipeline engineering around the world [1,2].

Welding is the most commonly used and effective way to make the cylinder-shaped pipeline in factories and join onshore pipes together on-site. The conventional welding methods used for pipeline steels, which have been studied abundantly [3], are mainly submerged arc, gas metal arc, shielded metal arc, and electrical resistance welding. Laser welding is a relatively new application with high efficiency and energy saving that has been used since the early 1960s [4]. Laser welding or hybrid welding, such as fiber laser-MAG hybrid welding, has been used in pipeline steels, showing great application prospects due to such advantages as flexibility, high energy density, and efficiency [5,6]. The heat input of laser welding can significantly affect the microstructure and mechanical properties of low-alloy high-strength steels [7–9], but relatively few reports have been made on laser welding of X80 pipeline steel.

Corrosion has been one of the most important failure styles for the pipeline, and the welded joint is more susceptible to corrosion because of the gradients in chemical composition, metallurgical microstructure, and residual stress among the weld metal (WM), fusion line, heat-affected zone (HAZ) and base metal (BM). The corrosion damage of
pipeline steels in or near the welded joints has been a research focus for decades [10,11]. Zhu and Xu found that the WM and BM were the most cathodic and anodic regions, respectively, by assessment of the galvanic corrosion interactions of the different regions in a CO\textsubscript{2}-containing environment [12]. Wang and Liu found that the microstructure of granular bainite mixed with ferrite and acicular ferrite showed the lowest and highest corrosion resistance, respectively, in X80 pipeline steel HAZ [13]. Ahmad et al. showed that grooving corrosion and rapid thinning are largely accelerated by welding defects, and the corrosion rate can be declined by alloying additions in WM, like Mo, Cr, V, and Mn [14]. Sajjad et al. found that proper heat treatment can promote the corrosion resistance of HAZ and WM in a high pH solution, which can be attributed to the formation of uniformly distributed polygonal ferrite and the decrease in the volume fraction of bainite [15]. Most of the previous corrosion tests were concentrated in soil, aqueous solution, sodium chloride solution, and seawater. In recent years, hydrogen sulfide corrosion inside the pipeline has attracted much attention. Such corrosion will cause stress corrosion and hydrogen cracking of the pipeline, seriously endangering its service life [16,17]. The research on content of hydrogen sulfide corrosion by relevant scholars mainly focuses on the base metal or traditional welded joints, but studies on laser welded joints of X80 pipeline steel are scant.

Therefore, in this study, X80 pipeline steel welded joints with different welding heat inputs were obtained by laser welding technology. The microstructure, mechanical properties, and corrosion resistance (in an H\textsubscript{2}S environment) were investigated. The effects of heat input and microstructure on corrosion resistance were also explored.

2. Experimental Procedures

2.1. Materials and Solutions

The chemical composition of X80 pipeline steels used in this study was (wt.%) 0.046C–0.305Si–1.76Mn–0.058Al–0.079Nb–0.008V–0.225Ni–0.023Cr–0.226Mo–0.015Ti–0.215Cu–0.00025B with low concentrations of S (0.007%) and P (0.001%). The CE\textsubscript{pcm}, adopted by American Petroleum Institute, was used to specify the limit of carbon equivalent (CE) for high-strength pipeline steel when the carbon mass fraction is less than 0.12%. Thus, the CE\textsubscript{pcm} for the X80 pipeline steel used in this study was 0.17693%.

The test solution used in this study was NACEA solution (Tianjin Kermel Chemical Reagent Co., Ltd., Tianjin, China), which contains 5 wt.% NaCl and 0.5 wt.% CH\textsubscript{3}COOH with saturated H\textsubscript{2}S at pH 2.8. The temperature was maintained at 50 °C during tests. Prior to the testing, the solution was purged with N\textsubscript{2} for 2 h, and H\textsubscript{2}S flow was maintained during the test duration.

2.2. The Laser Welding Process

The sample in this experiment was X80 pipeline steel with a size of 200 mm × 100 mm × 26.4 mm. After all sample surfaces were sanded, they were cleaned with ethanol and dried to ensure the same experimental conditions and uniform surface treatment. The welding process was carried out by fiber laser (IPG-YLS-10000, IPG Photonics Corporation, Oxford, MA, USA) with a maximum power of 10 kW, an emission wavelength of 1070 nm, and a spot focus diameter of 0.2 mm. The heat input was varied by controlling the welding speed under the premise of ensuring acceptable penetration and forming. A set of experiments was designed with five levels of welding heat input (2.86 to 6.67 kJ/cm) with a fixed power of 10 kW. In order to reduce the error of the experiment, each level was repeated three times. The experimental parameters are shown in Table 1. In the welding process, 99.99% argon shielding gas with a flow rate of 15 L/min was adopted. The angle between the gas flow direction and vertical middle line was 45°, and five heat input samples were processed in sequence perpendicular to the welding direction. A welding diagram is shown in Figure 1.
To better find the variation law of the microstructure, we selected samples S1, S3, and S5 for analysis, and the same is true for subsequent experiments. Image Pro Plus 6.0 (Media Cybernetics, Rockville, MD, USA) software was used to count the proportion of structures in each area of welded joints with different welding heat inputs according to the micromorphological characteristics of different microstructures. Microhardness measurements (HXD-1000TMC, Xian Weixin Testing Equipment Co., LTD., Xi’an, China) were performed under a loading force of 200 g and a loading time of 15 s. After measuring five different locations for each sample, the average was taken and each sample was replicated three times. Tensile tests were performed in accordance with American Society of Testing Materials (ASTM) E 8M-04 standards. The experiments were carried out using an electronic universal testing machine (Zwick-Z250, ZwickRoell GmbH & Co. KG, Ulm, Germany) with a sample size of 100 mm × 15 mm × 3 mm. The experiment was repeated five different locations for each sample, the average was taken and each sample was replicated three times to ensure the accuracy of the experimental results.

2.4. Electrochemical Measurements

Electrochemical polarization curves and electrochemical impedance spectroscopy are of great significance in metal corrosion research and have been widely cited. Through their measurement results, information of metals such as corrosion rate, corrosion kinetics, and corrosion mechanism can be analyzed and discussed. Therefore, in this paper, electrochemical technology was used to study the corrosion resistance of welded joints.

The test samples for electrochemical experiments were 5 mm × 5 mm × 2 mm cut from base material (BM), weld metal (WM), coarse-grained heat-affected zone (CGHAZ) and fine-grained heat-affected zone (FGHAZ) in welded joints, respectively. Prior to electrochemical tests, the samples were ground up to 800 grit SiC paper, then soldered to copper wires, mounted in silica gel, rinsed with deionized water, degreased in acetone, cleaned ultrasonically with ethyl alcohol for 15 min, and then air-dried.

Table 1. The specific experimental parameters in the laser welding procedures.

<table>
<thead>
<tr>
<th>No.</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>S5</th>
</tr>
</thead>
<tbody>
<tr>
<td>power/P (kW)</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>welding rate/v (cm/s)</td>
<td>3.5</td>
<td>3.0</td>
<td>2.5</td>
<td>2.0</td>
<td>1.5</td>
</tr>
<tr>
<td>heat input/E (kJ/cm)</td>
<td>2.86</td>
<td>3.33</td>
<td>4.00</td>
<td>5.00</td>
<td>6.67</td>
</tr>
</tbody>
</table>

Figure 1. Schematic diagram of fiber laser welding.
A three-electrode electrochemical cell system was employed with the use of the studied material as the working electrode (Gamry Interface 1000, Gamry Instruments Consulting Co., Ltd., Shanghai, China), platinum plate as the counter electrode, and saturated calomel electrode (SCE, Gamry Instruments Consulting Co., LTD., Shanghai, China) of +0.241 V \text{SHE} as the reference electrode. The electrochemical experiments were conducted after there was almost no change in open circuit potential (OCP) to assure the stability and validity. Electrochemical impedance spectroscopy (EIS) tests were performed at the OCPs from 0.01 Hz to 100 kHz with an amplitude of 10 mV. AC impedance spectrum curves of immersion for 0 h and 96 h were measured and the potentiodynamic polarization curves were obtained at 0.5 mV/s sweep rate.

3. Results
3.1. Microstructure Evolution

As shown in Figure 2, the cross sections of the welded joints presented similar sound profiles with typical “goblet” shape without cracks and of acceptable appearance, indicating the feasibility of the welding processes with five welding speeds. The fusion line and the boundaries between heat-affected zone (HAZ) and BM (embellished by dashed lines) can be observed clearly. The welding penetration and width increased linearly with the increase in heat input, while their ratio decreased from about 1.9 to 1.3 (Figure 3).

![Figure 2. Optical microscopy of weld cross sections with different heat inputs of (a) 2.86, (b) 3.33, (c) 4.00, (d) 5.00 and (e) 6.67 kJ/cm.](image)

![Figure 3. The size of weld penetration, width and the ratio of weld penetration/width.](image)
In addition, a slight undercut was detected in the weld bead and its extent decreased or even disappeared with the increase in heat input. However, when the heat input increased to 6.67 kJ/cm, a hole was detected in the center of the weld bead, which was attributed to metal evaporation and gravitational effects.

The microstructures of the welded joints with three different heat inputs are shown in Figures 4–6. It can be seen that their microstructures undergo a series of transformations from the weld metal to the BM.

![Figure 4. Microstructure of the X80 pipeline steel welded joint with the heat input of 2.86 kJ/cm: (a) welded metal; (b) CGHAZ; (c) FGHAZ and (d) BM.](image)

The microstructure of the as-received BM was polygonal ferrite (PF) with fine equiaxed grains and granular bainite (GB) with embellished by martensite (M) plates and retained austenite (so called M/A islands) as the secondary phase. The microstructure characteristics were formed by thermomechanically controlled processing (TMCP) [18]. The uniform distribution of fine mild microstructure of PF and hard microstructure of GB gives the pipeline steel better performance, including high deformability in particular.

In the WM with different heat inputs, the types and sizes of microstructure vary widely. The microstructure transforms from low-carbon martensite with lath spacing less than 1 µm to fine-grained acicular ferrite with the increase in heat input, and bainite (B) changes from lath to granular. In addition, the M/A composition also changed from chains to islands and was evenly distributed around the ferrite (F) grains.
In addition, a slight undercut was detected in the weld bead and its extent decreased or even disappeared with the increase in heat input. However, when the heat input increased to 6.67 kJ/cm, a hole was detected in the center of the weld bead, which was attributed to metal evaporation and gravitational effects.

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**Figure 4.** Microstructure of the X80 pipeline steel welded joint with the heat input of 2.86 kJ/cm: (a) welded metal; (b) CGHAZ; (c) FGHAZ and (d) BM.

**Figure 5.** Microstructure of the X80 pipeline steel welded joint with the heat input of 4 kJ/cm: (a) welded metal; (b) CGHAZ and (c) FGHAZ.

**Figure 6.** Microstructure of the X80 pipeline steel welded joint with the heat input of 6.67 kJ/cm: (a) welded metal; (b) CGHAZ and (c) FGHAZ.

The microstructure of the as-received BM was polygonal ferrite (PF) with fine equiaxed grains and granular bainite (GB) with embellished by martensite (M) plates and retained austenite (so called M/A islands) as the secondary phase. The microstructure characteristics were formed by thermomechanically controlled processing (TMCP) [18]. The uniform distribution of fine mild microstructure of PF and hard microstructure of GB gives the pipeline steel better performance, including high deformability in particular.

In the WM with different heat inputs, the types and sizes of microstructure vary widely. The microstructure transforms from low-carbon martensite with lath spacing less than 1 μm to fine-grained acicular ferrite with the increase in heat input, and bainite (B).

In the CGHAZ with different heat inputs, a similar granular bainite was obtained and the coarse prior austenite grain boundaries (PAGB) (embellished by dashed lines)
embellished by M/A islands was observed clearly. The bainitic ferrite matrix was lath-shaped and the M/A islands disperses in the boundaries of ferrite lath grains. The ferrite lath width increased and the M/A islands changed from needle-like to granular as the heat input increased.

In the FGHAZ with different heat inputs, the type of microstructure did not change, consisting mainly of massive ferrite and granular bainite interspersed with M/A islands.

The microstructure ratios of the base metal and each area of the welded joint with different heat input were counted, and the results are shown in Figure 7. The microstructure proportions of ferrite and bainite in the base metal are 91.7% and 8.3%, respectively. The largest proportion of the microstructure in each region of the joint is ferrite. When the heat input is 6.67 kJ/cm, the proportion of ferrite in FGHAZ is as high as 87.9%. With the increase in heat input, the proportion of ferrite in each region increases, and the sum of the proportion of martensite and bainite decreases. The proportion of bainite in WM and CGHAZ increases, the proportion of martensite decreases, and the proportion of bainite in FGHAZ decreases. The microstructure ratios of different regions of the welded joints are also quite different, with the largest proportion of ferrite in FGHAZ and the smallest in WM, while the sum of the proportions of martensite and bainite is the opposite.

![Figure 7. Histograms of microstructure proportion of welded joints with different heat inputs: (a) welded metal; (b) CGHAZ and (c) FGHAZ.](image)

### 3.2. Mechanical Properties of Welded Joint

The nominal stress–strain curves of the X80 pipeline steel and its laser welded joint with different welding rates are presented in Figure 8. The results of ultimate tensile strength, yield strength and elongation are shown in Table 2. Almost no difference can be seen in the elastic region; the obvious strain-hardening behaviors can be seen for all samples. The laser welding thermal cycle has a conducive effect on the engineering strength, including the yield strength and the tensile strength, detrimental to the ductility. The strength and elongation also increased as the heat input increased.
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Figure 8. Nominal stress–strain curves of the X80 pipeline steel and its welded joint.

Table 2. Tensile test results of welded joints.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ultimate Tensile Strength (MPa)</th>
<th>Yield Strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>789</td>
<td>565</td>
<td>19.37</td>
</tr>
<tr>
<td>2.86 kJ/cm</td>
<td>750</td>
<td>620</td>
<td>7.49</td>
</tr>
<tr>
<td>4.00 kJ/cm</td>
<td>774</td>
<td>641</td>
<td>8.8</td>
</tr>
<tr>
<td>6.67 kJ/cm</td>
<td>870</td>
<td>720</td>
<td>11.6</td>
</tr>
</tbody>
</table>

The observed microstructure variations occurring during the welding are clearly reflected in the microhardness distribution symmetrically. Figure 9 demonstrates some typical results. The hardness decreases gradually from the weld to the base metal, and the hardness value in the weld area decreases gradually with the increase in heat input.

Figure 9. The microhardness of the welded joints with different heat inputs.
3.3. Electrochemical Characterization

3.3.1. Potentiodynamic Polarization

Figure 10 shows the potentiodynamic polarization curves of each region of the welded joint with different welding heat inputs in NACEA solution saturated with hydrogen sulfide. The results showed that their anodic and cathodic processes were controlled by the charge transfer process, and no passivation process occurred. The Tafel extrapolation method was used for fitting to obtain the corrosion potential (E\text{corr}) and corrosion current density (i\text{corr}). The fitting results are shown in Table 3 and Figure 11. The more positive the value of E\text{corr}, the smaller the corrosion driving force, and the smaller the value of i\text{corr}, the lower the corrosion rate of the material [19–22]. With the increase in heat input, the E\text{corr} of each region of the welded joint shifted to the positive direction, and the E\text{corr} of WM was most affected by the welding heat input, rising from $-677.6$ mV to $-627.8$ mV, followed by FGHAZ and CGHAZ. The i\text{corr} of each region of the welded joint also showed a downward trend with the increase in heat input, and the i\text{corr} of the FGHAZ metal was smaller than that of the base metal when the heat input was 6.67 kJ/cm. The E\text{corr} in different regions of the welded joint with different heat inputs showed the same variation law: the E\text{corr} of FGHAZ was the most positive, and the E\text{corr} of CGHAZ was the most negative. An increase in heat input reduced the corrosion driving force and corrosion rate in various regions of the welded joint, similar to the findings of Huang et al. [21].

Figure 10. The potentiodynamic polarization curves of base material and fusion materials of laser welding with different heat inputs in NACEA solution with saturated H\textsubscript{2}S: (a) 2.86; (b) 4 and (c) 6.67 kJ/cm.
Table 3. Electrochemical parameters fitted from polarization curves.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ecorr (mV)</th>
<th>icorr (µA/cm²)</th>
<th>βα (mV dec⁻¹)</th>
<th>ββ (mV dec⁻¹)</th>
<th>Corrosion Rate (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>-638.4</td>
<td>105.2</td>
<td>471.0</td>
<td>163.1</td>
<td>47.8</td>
</tr>
<tr>
<td>S1</td>
<td>-677.6</td>
<td>677.9</td>
<td>113.6</td>
<td>216.6</td>
<td>308.1</td>
</tr>
<tr>
<td>WM</td>
<td>-722.1</td>
<td>1058.4</td>
<td>618.1</td>
<td>312.1</td>
<td>481.0</td>
</tr>
<tr>
<td>CGHAZ</td>
<td>-630.2</td>
<td>254.0</td>
<td>118.8</td>
<td>317.5</td>
<td>115.5</td>
</tr>
<tr>
<td>FGHAZ</td>
<td>-669.3</td>
<td>238.1</td>
<td>125.9</td>
<td>159.7</td>
<td>108.2</td>
</tr>
<tr>
<td>S3</td>
<td>-714.6</td>
<td>683.9</td>
<td>589.4</td>
<td>237.4</td>
<td>310.7</td>
</tr>
<tr>
<td>WM</td>
<td>-621.5</td>
<td>176.3</td>
<td>119.8</td>
<td>312.2</td>
<td>80.1</td>
</tr>
<tr>
<td>CGHAZ</td>
<td>-627.8</td>
<td>169.2</td>
<td>248.9</td>
<td>176.7</td>
<td>76.9</td>
</tr>
<tr>
<td>FGHAZ</td>
<td>-699.3</td>
<td>482.7</td>
<td>256.1</td>
<td>189.3</td>
<td>219.3</td>
</tr>
<tr>
<td>S5</td>
<td>-603.3</td>
<td>68.9</td>
<td>118.8</td>
<td>123.6</td>
<td>31.3</td>
</tr>
</tbody>
</table>

3.3.2. Electrochemical Impedance Spectroscopy

Figure 12 shows the electrochemical impedance spectroscopy results for each sample in a hydrogen sulfide-saturated NACEA solution. The Nyquist plot consists of capacitive reactance arcs in the first quadrant and inductive reactance arcs in the fourth quadrant, indicating that pitting corrosion occurs at this time [23]. An $R_s(C_{dl} R_{ct}(LR_L))$ equivalent circuit was used to fit the results, in which $R_s$ was the solution resistance, $C_{dl}$ was the double-layer capacitor, $R_{ct}$ was the charge transfer resistance, $L$ was the sense resistance, and $R_L$ was the sense resistance fitting. The results are shown in Table 4 and Figure 13. With the increase in heat input, the charge transfer resistance $R_{ct}$ in each region of the welded joint showed an upward trend, the $R_{ct}$ of the FGHAZ metal increased from 216.2 $\Omega\cdot$cm² to 412.5 $\Omega\cdot$cm², and the value increases of CGHAZ and WM were also more than 100 $\Omega\cdot$cm². Moreover, the size of $R_{ct}$ in each area of the joint with different heat inputs was expressed as CGHAZ < WM < FGHAZ. The larger the value of $R_{ct}$, the higher the resistance of the sample and the better the corrosion resistance [24], consistent with the result of the polarization curve.
Figure 12. EIS results for 0 h immersion of BM and different zones in laser welded joints in NACEA solution with saturated H$_2$S at 50°C: (a) 2.86; (b) 4 and (c) 6.67 kJ/cm.

Table 4. The fitted values of EIS for different samples under immersion for 0 h.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$R_\text{s}$ (Ω·cm$^2$)</th>
<th>$C_{\text{dl}}$ (μF·cm$^{-2}$)</th>
<th>$R_{\text{ct}}$ (Ω·cm$^2$)</th>
<th>$L$ (H·cm$^{-2}$)</th>
<th>$R_L$ (Ω·cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>3.55</td>
<td>21.85</td>
<td>326.1</td>
<td>3586</td>
<td>1092</td>
</tr>
<tr>
<td>S1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WM</td>
<td>3.61</td>
<td>36.58</td>
<td>103.2</td>
<td>3012</td>
<td>516</td>
</tr>
<tr>
<td>CGHAZ</td>
<td>3.58</td>
<td>41.52</td>
<td>35.6</td>
<td>3862</td>
<td>216</td>
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<tr>
<td>FGHAZ</td>
<td>3.46</td>
<td>28.12</td>
<td>216.2</td>
<td>2815</td>
<td>883</td>
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<tr>
<td>S3</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>WM</td>
<td>3.66</td>
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<td>612</td>
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<td>356</td>
</tr>
<tr>
<td>FGHAZ</td>
<td>3.59</td>
<td>25.65</td>
<td>267.5</td>
<td>2965</td>
<td>985</td>
</tr>
<tr>
<td>S5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WM</td>
<td>3.38</td>
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<td>279.5</td>
<td>3125</td>
<td>815</td>
</tr>
<tr>
<td>CGHAZ</td>
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<td>30.15</td>
<td>139.6</td>
<td>3016</td>
<td>389</td>
</tr>
<tr>
<td>FGHAZ</td>
<td>3.61</td>
<td>18.77</td>
<td>412.5</td>
<td>3069</td>
<td>1563</td>
</tr>
</tbody>
</table>
Figure 12. EIS results for 0 h immersion of BM and different zones in laser welded joints in NACE Ae solution with saturated H2S at 50°C: (a) 2.86; (b) 4 and (c) 6.67 kJ/cm.

Figure 13. Fitting results of $R_{ct}$ extracted from impedance spectrum curves of different samples.

Figure 14 shows the electrochemical impedance spectroscopy results of different heat input welding joints after immersion in NACE Ae solution saturated with hydrogen sulfide for 96 h. The Nyquist diagrams were composed of capacitive reactance arcs in the first quadrant, without inductive reactance arcs. An $R_{s}(Q_{f}(R_{ct}C_{dl}R_{f})))$ equivalent circuit was used to fit the results. In the circuit, $R_{s}$ was the solution resistance, $C_{dl}$ was the double-layer capacitor, $Q_{f}$ was the constant phase element of the corrosion products, $R_{ct}$ was the charge transfer resistance, and $R_{f}$ was the resistance of the corrosion products. The fitting results are shown in Table 5 and Figure 15. The effect of heat input on $R_{f}$ and $R_{ct}$ was the same as that without immersion, and the order of corrosion resistance in each region did not change. However, the $R_{ct}$ was elevated for each of the samples compared with the unimmersed state, indicating an increase in corrosion resistance, which was attributed to a film of sulfide corrosion products developed on the surface of the samples [25,26].

Table 5. The fitted values of EIS for different samples under immersion for 96 h.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$R_{s}$ ($\Omega \cdot cm^{2}$)</th>
<th>$Y_{0}$ (S$^{-1} \cdot cm^{2} \cdot S^{n}$)</th>
<th>$n_{dl}$</th>
<th>$R_{f}$ ($\Omega \cdot cm^{2}$)</th>
<th>$C_{dl}$ ($\mu F \cdot cm^{-2}$)</th>
<th>$R_{ct}$ ($\Omega \cdot cm^{2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>7.56</td>
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<td>0.5654</td>
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Figure 14 shows the electrochemical impedance spectroscopy results of different heat input welding joints after immersion in NACE A solution saturated with hydrogen sulfide for 96 h. The Nyquist diagrams were composed of capacitive reactance arcs in the first quadrant, without inductive reactance arcs. An R\( _s \) (Q\( _f \) (R\( _{ct} \) (C\( _{dl} \) R\( _f \))) \) equivalent circuit was used to fit the results. In the circuit, R\( _s \) was the solution resistance, C\( _{dl} \) was the double-layer capacitor, Q\( _f \) was the constant phase element of the corrosion products, R\( _{ct} \) was the charge transfer resistance, and R\( _f \) was the resistance of the corrosion products. The fitting results are shown in Table 5 and Figure 15. The effect of heat input on R\( _f \) and R\( _{ct} \) was the same as that without immersion, and the order of corrosion resistance in each region did not change. However, the R\( _{ct} \) was elevated for each of the samples compared with the unimmersed state, indicating an increase in corrosion resistance, which was attributed to a film of sulfide corrosion products developed on the surface of the samples [25,26].

Figure 14. EIS results for 96 h immersion of BM and different zones in laser welded joints in NACE A solution with saturated H\( _2 \)S at 50 °C: (a) 2.86; (b) 4 and (c) 6.67 kJ/cm.

Figure 15. Fitting results of R\( _{ct} \) and R\( _f \) extracted from impedance spectrum curves of different samples: (a) heat input and R\( _{ct} \) change line chart; (b) heat input and R\( _f \) change line chart.

4. Discussion

4.1. Effect of Heat Input on Microstructure

The main feature of laser welding is rapid heating and cooling during the thermal cycle of the welded joint. During the thermal cycle of welded joints, due to the different distances from the heat source, the microstructure is affected by the thermal cycle to a different degree, and the phase transition mode is different, so the type, content, and size of the formed microstructure are different [27–29]. During welding, austenitic transformation occurs due to heat input, and then, it will be cooled down in the air with different cooling rates depending on the heat input values. Different cooling rates lead to differences in microstructure [30,31].

The peak temperature of WM is above the liquidus line, so the metal in this region undergoes heating, phase transition, melting, solidification, and solid phase transition. When the heat input was small, the cooling rate was fast, the residence time at high
temperatures was very short, and the carbon atoms in the structure had no time to diffuse and directly shear into lath martensite [32]. As the heat input increased, the cooling rate decreased, the stability of the austenite decreased, and the carbon atoms had sufficient time to diffuse, resulting in an increased in ferrite and bainite. The CGHAZ was closer to the weld, and the peak temperature was higher during the welding thermal cycle, and the austenite grains grew sharply. Finally, in the process of rapid cooling, coarse martensite and ferrite microstructures were obtained, and the microstructure was extremely inhomogeneous. With the increase in heat input, the cooling rate increased, the driving force of ferrite grain nucleation decreased, and finally lath-like bainite was formed [33]. Given that FGHAZ has a lower peak temperature, it was equivalent to a normalizing heat treatment. After the phase transformation and recrystallization, the austenite was mostly transformed into ferrite. Considering that the formation of ferrite was a process of carbon emission, the final phase transformed austenite has a higher carbon content and formed granular bainite, and the microstructure was uniformly refined [34].

4.2. Effect of Heat Input on Mechanical Properties

The heat input mainly affects the mechanical properties by affecting the type and morphology of the microstructure. Generally, the toughness and plasticity of ferrite are higher than those of bainite and martensite, while martensite has the highest hardness, followed by bainite and ferrite [35–37]. Grain refinement also plays a large role in improving the strength of the material [38,39]. The structure of the base metal is mainly ferrite, so the hardness is the lowest and the elongation is the highest. With the increase in heat input, the coarse martensite in the welded joint gradually decreases and disappears, the content of ferrite increases, and the grains gradually becomes finer. Therefore, with the increase in heat input, the strength increases and the elongation decreases. Compared with other regions, the proportion of martensite and bainite in WM is higher, so the hardness is the highest. As the heat input increases, the content of martensite and bainite decreases, and the hardness also decreases [40]. FGHAZ is mainly composed of ferrite and bainite, which is quite different from the martensite structure in CGHAZ, so the hardness is below it.

4.3. Effect of Heat Input on Corrosion Resistance

X80 pipeline steel is a low-carbon and low-alloy steel, and its corrosion resistance is greatly affected by the microstructure. The type, proportion, and grain size of the microstructure all play a crucial role in corrosion resistance [41,42]. High welding heat input can increase the balance of the welded joint structure, increase the content of ferrite, and reduce the content of martensite and bainite, thereby improving corrosion resistance [42]. Each area of the welded joint also has different corrosion resistance due to different microstructures [43]. The difference in microstructure makes the $E_{corr}$ of each area different, and a galvanic effect is formed at the junction of the areas, so that the area with negative $E_{corr}$ is preferentially corroded while the $E_{corr}$ of the value is related to Kelvin potential. The larger the Kelvin potential, the larger the $E_{corr}$. The relationship between them is shown in Equation (1).

$$E_{corr} = \left( \frac{W_{ref}}{F} - \frac{E_{ref}}{2} \right) + \varphi$$

where $W_{ref}$ represents the work function for the reference electrode, $\frac{E_{ref}}{2}$ represents the half-cell potential of the reference electrode, $F$ represents the Faraday constant, and $\varphi$ represents the Kelvin potential.

Ferrite has a higher Kelvin potential, followed by bainite and martensite [44]. WM and CGHAZ have more martensite and bainite content, but CGHAZ has the worst corrosion resistance, which is due to coarse grains and irregular structure, aggravating the corrosion tendency [45–47]. FGHAZ is mainly composed of ferrite and granular bainite. The $E_{corr}$ value tends to be positive, the grain size is fine, the structure is uniform, and the corrosion resistance is good.
To sum up, different welding heat input results in changes in the proportion of microstructure in each area of the welded joint, and the difference in microstructure leads to the difference in corrosion rate. The proportion of ferrite and the amount of heat input, the ratio of $i_{corr}$ to ferrite, and the ratio of $R_{ct}$ to ferrite were linearly fitted to obtain their functional models. The fitting results are shown in Figure 16a–c.

![Data-fitting curve](image)

**Figure 16.** Data-fitting curve: (a) fitting diagram of heat input and ferrite proportion function, (b) functional model of ferrite proportion and $i_{corr}$, (c) functional model of ferrite proportion and $R_{ct}$, (d) function model of heat input and $i_{corr}$, (e) function model of heat input and $R_{ct}$. 
Combined with their fitting results, the functional models of heat input and \( i_{\text{corr}} \) and \( R_c \) can be obtained, respectively, as shown in Figure 16d,e. The magnitudes of the slopes in the two figures clearly show that the welding heat input has a greater effect on the corrosion rate in the CGHAZ region, followed by WM and FGHAZ. Similarly, the correlation function model of heat input and the sum of the proportions of martensite and bainite can be obtained.

Figure 17 is a schematic diagram of the reaction of the welded joint immersed in H\(_2\)S saturated NACEA solution. The figure indicates the reactions occurring during immersion can be divided into anodic, cathodic, and other reactions [25,26].

**Figure 17.** Schematic of the formation process of sulfide film on X80 pipeline steel surface after immersion in NACEA solution with saturated H\(_2\)S gas at 50 °C.

When immersed for 0 h, the anodic reaction dissolved the surface of the steel to produce Fe\(^{2+}\) and released it into the corrosion solution, reducing the thickness of the steel [41,48]. With the progress of the reaction, the formation rate of the corrosion product mackinawite increased due to the increase of Fe\(^{2+}\) and S\(^{2-}\) in the electrolyte. However, because the rate of the synthesis reaction was much smaller than that of the anodic reaction, the corrosion products would not cover the surface of the substrate and are loose and fall off easily [17,49,50]. At the same time, H in the solution may also lead to hydrogen permeation. The hydrogen permeation is defined as the process where hydrogen atoms (H) adsorbed on the outer surface (H\(_{\text{ads}}\)) of a metal enter the metal, become absorbed on the inner surface (H\(_{\text{abs}}\)). Some H\(_{\text{abs}}\) produced by the cathode are chemically or electrochemically bound, adsorbed on the metal surface or leave as H\(_2\). A part of H\(_{\text{ads}}\) enters the metal to become H\(_{\text{abs}}\). Some H\(_{\text{abs}}\) accumulate inside the metal or in hydrogen traps, such as vacancies, dislocations, grain boundaries, and phase interfaces, embrittling the metal surface and exacerbating corrosion [51,52]. The presence of Cl\(^-\) in the solution would also promote the progress of the anodic reaction and the formation of pitting holes, so the inductive arc appeared in Figure 11. During the reaction, these pitting pores act as anodes, attracting the gradual accumulation of S\(^{2-}\), HS\(^-\), and Cl\(^-\) [25].

With the prolongation of immersion time, the reaction of corrosion product synthesis accelerated, corrosion products gradually accumulated, and two interfaces, namely, Fe/FeS interface and FeS/solution interface, were gradually formed [53,54]. The corrosion product at this time is a mixture of mackinawite and cubic ferrous sulfide [25,50]. Some Fe\(^{2+}\) produced by the dissolution of Fe reacted with ferrous sulfide, hydrogen sulfide, HS\(^-\), and
$S^2^−$ to form a new type of sulfide film with relatively rich iron and low S content at the Fe/FeS interface. At this time, the corrosion products are relatively dense. In addition, other $Fe^{2+}$ ions were released into the solution through the sulfide film and reacted with hydrogen sulfide, HS$^−$, and $S^2^−$, resulting in the continuous coating of corrosion products on the steel surface [55]. The sulfide film also reacted with hydrogen sulfide, HS$^−$ and $S^2^−$ at the FeS/solution interface. Therefore, the thickness of the sulfide film increases at the FeS/solution interface, leading to an increase in $R_f$ [25]. At the same time, it prevents corrosion products such as Cl$^−$ and $H_{abs}$ from entering the substrate. The reaction of $S^2^−$, HS$^−$, and $Fe^{2+}$ accumulating in the pitting pits resulted in the precipitation of ferrous sulfide corrosion products on the walls of the pitting pits, finally filling the pitting pits [25,30]. Therefore, after immersion for 96 h, a dense corrosion products film was formed on the surface of the substrate, causing the corrosion difference from immersion for 0 h, increased $R_{ct}$, and enhanced corrosion resistance.

5. Conclusions

In this study, X80 pipeline steel welded joints with different heat inputs were obtained by laser welding, and their microstructure, mechanical properties, and corrosion resistance (in saturated $H_2S$ NACEA solution) were analyzed. The following conclusions were obtained.

1. With the increase in heat input, the proportion of ferrite in each area of the welded joint gradually increased, the sum of the proportion of martensite and bainite decreased, the proportion of bainite in WM and CGHAZ increased, and the proportion of martensite structure decreased, the microstructure type of FGHAZ has changed very little.
2. With the increase in heat input, the strength and elongation increased, and the hardness of the weld center decreased.
3. The electrochemical results show that the corrosion resistance of welded joints increased with the increase in heat input, and the structure of FGHAZ is the least easily corroded in each area of welded joints, followed by WM and CGHAZ. The function models of heat input size and $i_{corr}$ and $R_{ct}$ values were established. In addition, the corrosion product film produced by the long-term immersion of the welded joint in the saturated $H_2S$ NACEA solution can hinder the development of corrosion and enhance the corrosion resistance to a certain extent.

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