Pickling behavior of 2205 duplex stainless steel hot-rolled strips in mixed solutions of HNO₃-HF

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Keywords: 2205 duplex stainless steel, HNO₃-HF, corrosion potential, pickling, electrochemical impedance spectroscopy

Abstract
The pickling behaviour of 2205 DSS hot-rolled strips after annealing and sand blasting was studied in the mixed solutions of HNO₃-HF using weight loss rate, surface analysis, corrosion potential, and electrochemical impedance spectroscopy measurements. The pickling rate decreased as the concentration of HNO₃ increased in the mixed solutions of HNO₃ + 25 g l⁻¹ HF (x = 40 ÷ 200 g l⁻¹) at 50 °C due to passivation. The passivating effect of HNO₃ became weak as its concentration was less than 80 g l⁻¹. The pickling rate increased noticeably when the concentration of HF in the mixed solutions of 120 g l⁻¹ HNO₃ + y HF (y = 5 ÷ 80 g l⁻¹) at 50 °C was increased. The dissolution of the metal under the oxide scale may have changed from the passive state to the active state as the HF concentration was higher than 25 g l⁻¹. The pickling dissolution accelerated noticeably as the temperature rose from 40 to 60 °C. With the optimised pickling process, 2205 DSS hot-rolled strips can be pickled industrially with good efficiency and surface topography.

1. Introduction
Type 2205 duplex stainless steels (DSSs) are promising materials owing to their excellent mechanical behaviour and high corrosion resistance [1, 2]. The excellent mechanical behaviour allows for a lighter construction, less welding, and more compact system design [3, 4]. The high corrosion resistance ensures more service time than that of the conventional stainless steels [5–9]. The demand for 2205 DSS has been quickly increasing in the field of chemical, nuclear, transportation, construction, oil, and gas industries [10]. However, the production of 2205 DSS has been greatly restricted by its pickling process [11].

The pickling process is used to remove the oxide scales and chromium-depleted layers which form on the surface of stainless steels during high-temperature processing [12, 13]. The industrial pickling process of stainless steel includes mechanical descaling, pre-pickling, and mixed-acid pickling. A mechanical descaling is achieved through breaking, grinding, roto blasting, and sand blasting processes. Pre-pickling may be used in acidic or neutral electrolytes with certain current densities to enhance the pickling performance [14–25]. Mixed-acid pickling is the final step to dissolve the oxide scales and improve the surface topography.

Mixed-acid pickling plays an important role in the industrial production processes of 2205 DSS. The common mixed-acid solutions are H₂SO₄-HF, H₂SO₄-HNO₃, H₂PO₄-H₂SO₄, HCl-HF, and HNO₃-HF. While these mixed-acid solutions have remarkable properties, they do, however, have certain downsides. Specifically, while the mixed-acid solutions of H₂SO₄-HF are effective for the pickling of the 304 stainless steels, they are not suitable for those with poor corrosion resistance [18]; while H₂PO₄-H₂SO₄ solutions have good properties of dissolving oxide scales on the surface of most stainless steels, they are, however, expensive [26]; while H₂SO₄-HNO₃ solutions have good pickling ability, they easily emit pollutant nitrogen gases; and while HCl-HF solutions quickly dissolve oxide scales on the surface of most stainless steels, their chloride ions may reduce the corrosion resistance of stainless steels [20]. The HNO₃-HF solutions are traditionally applied due to their excellent quality and low cost of production [27].
3. Results

3.1. Characterisation of oxide scales

A common characteristic of the oxide layers is double-oxide stratification, with regions closer to the matrix exhibiting higher concentrations of chromium oxide [29]. The inner oxides mainly contained Cr₂O₃ ⋅ FeO, NiO ⋅ Fe₂O₃, Fe₃CrO₄, Fe₅Cr₂O₈, and Fe₅SiO₄ [30, 31]. As shown in figure 1, a few oxide scales remained on the surface of the test specimens after most oxide scales were broken and peeled by the sand blasting. The results of the Raman spectroscopy in figure 2 indicate that the oxides on the surface of the test specimens are Fe₂O₃, Fe₃O₄, and Cr₂O₃ (i.e., MnCr₂O₄, NiCr₂O₄, and FeCr₂O₄) [32–34]. Among them, the content of MCr₂O₄ had the highest peak.

3.2. Pickling of the different HNO₃ concentrations

The weight loss rates (i.e., pickling rates), typical surface images, and EDS analyses after pickling in the mixed solutions of x g L⁻¹ HNO₃ + 25 g L⁻¹ HF at 50 °C (x = 40 ~ 200) are shown in figures 3 and 4 and table 2, respectively. It can be seen that the weight loss rate decreased and the composition of the remaining oxides did not show clear changes in composition when the concentration of HNO₃ increased. Moreover, there was a transition at about 80 g L⁻¹ HNO₃. In the solution with 40 g L⁻¹ HNO₃, the weight loss rate had the largest value at approximately 1.72 g m⁻² min⁻¹ and had evidently few oxide scales that remained on the surface. On the other hand, the solution with 200 g L⁻¹ HNO₃ had the smallest weight loss rate at approximately 0.79 g m⁻² min⁻¹ and had many remaining oxide scales on the surface of the specimen. It was apparent that the pickling efficiency of 2205 DSS had a negative correlation with the HNO₃ concentration.

| C   | Si  | Mn  | S   | P   | Cr | Ni  | Mo  | N  |
|-----|-----|-----|-----|-----|----|-----|-----|----|
| 2205DSS | 0.024 | 0.62 | 1.42 | 0.001 | 0.024 | 21.13 | 5.46 | 3.11 | 0.15 |

The pickling of 2205 DSS is more difficult than those of traditional austenitic and ferritic stainless steels because of the following aspects: firstly, the oxide scales on the 2205 DSS surface are stable and dense due to its high chromium, molybdenum, and nitrogen contents [28]. Secondly, the nodular oxides often grow on the surface of the 2205 DSS hot-rolling strips because of the different oxidation rates of the ferrite and austenite phases at high temperatures [12]. Thirdly, the matrix of 2205 DSS dissolves evidently slowly in acidic solutions due to its excellent corrosion resistance. Therefore, the pickling of 2205 DSS is of practical significance.

The pickling technology and pickling mechanism are well known for their applications in austenitic and ferritic stainless steels; however, there are little to no systematic reports which focus on the pickling of 2205 DSS. In this study, the pickling behaviour of 2205 DSS hot-rolled strips was analysed in the mixed solutions of HNO₃-HF. The pickling performance was discussed based on pickling rate, surface morphology, corrosion potential, and impedance.

2. Experimental

A hot-rolled 2205 DSS strip with a thickness of 4.0 mm was used as the test materials. Its chemical composition is given in table 1.

A 300 × 300 mm plate was cut from the strip and annealed at 1140 °C for 4 min. After annealing, the plate was taken out from the furnace and cooled down in air. Then, the annealed plate was subjected to sand blasting to remove its main oxides. The above plate was cut into 20 × 30 mm test specimens. All test specimens were cleaned with alcohol and distilled water.

The corrosion potential and electrochemical impedance spectroscopy (EIS) of the test specimens were measured during the pickling process with a Princeton potentiostat (VMP3). Each specimen was fixed on the cell sidewall with a 1 cm² round hole. The test specimen was used as the working electrode; the platinum sheet was used as the counter electrode; and the Hg/HgSO₄ was used as the reference electrode (MSE).

Pickling tests were carried out with beakers in the thermostat water bath. An analytically pure HNO₃, HF, and de-ionised water were used to prepare the mixed-acid solutions. All test specimens were immersed in the mixed-acid solutions for 8.8 min. Each test specimen was weighed with a precision of 0.01 mg before and after pickling. The specimens were characterised using scanning electron microscopy (SEM, Fei-qunta600, Zeiss EVO MA25) and Raman spectroscopy (Renishaw, INVIA).

Table 1. Chemical composition of the 2205 DSS specimens (wt%).
The pickling processes in the mixed solutions of HNO₃-HF can display active or passive corrosion states. The oxides and chromium-depleted layers are easily dissolved under active states. On the contrary, the formation of passive films can inhibit the metal dissolution. These can be characterised by the electrochemical measurement techniques.

Figure 5 gives the corrosion potential in the mixed solutions of $x$ g l$^{-1}$ HNO₃ + 25 g l$^{-1}$ HF ($x = 40, 80, 120$ and $200$) at 50°C. When the concentration of HNO₃ was less than 80 g l$^{-1}$, the corrosion potential quickly declined at the beginning of the immersion and subsequently remained constant (approximately lower than $-360$ mV$\text{MSE}$) as the immersion time increased. On the other hand, when concentration of HNO₃ was larger than 120 g l$^{-1}$, the corrosion potential remarkably increased with the increasing immersion time and also reached the steady corrosion state with stable values higher than approximately 180 mV$\text{MSE}$.

Figures 6 and 7 shows the Nyquist and Bode plots respectively in the mixed solutions of $x$ g l$^{-1}$ HNO₃ + 25 g l$^{-1}$ HF ($x = 40, 80, 120$, and $200$) at 50°C under the $E_{corr}$ conditions (i.e., the free corrosion states). The semicircle size enlarged noticeably with the concentration of HNO₃ increasing from 40 to 120 g l$^{-1}$, but changed slightly as the concentration of HNO₃ was more than 120 g l$^{-1}$. The phase angle $\theta$ values increased.

Figure 1. Surface images of the test specimens.

Figure 2. Raman spectroscopy results of the test specimens.
Figure 3. Pickling rate of the specimens in the solutions of $x \text{ g L}^{-1} \text{ HNO}_3 + 25 \text{ g L}^{-1} \text{ HF}$ ($x = 40 \sim 200$) at $50^\circ$C.

Figure 4. SEM surface micrographs and EDS analyses after pickling in the mixed solutions of $x \text{ g L}^{-1} \text{ HNO}_3 + 25 \text{ g L}^{-1} \text{ HF}$ at $50^\circ$C: (A) $x = 40 \text{ g L}^{-1}$, (B) $x = 120 \text{ g L}^{-1}$ and (C) $x = 200 \text{ g L}^{-1}$; (a)–(c) are the local magnification areas for (A)–(C).

Table 2. EDS analyses of the positions in figure 4 (wt%).

| Position | O  | Cr | Mn | Fe  | Ni  |
|----------|----|----|----|-----|-----|
| a1       | 30.13 | 10.70 | 7.48 | 47.89 | 3.80 |
| a2       | 32.75 | 32.51 | 6.87 | 25.96 | 1.92 |
| b1       | 35.94 | 10.28 | 4.09 | 45.63 | 4.06 |
| b2       | 33.39 | 36.41 | 4.14 | 24.87 | 1.18 |
| c1       | 35.84 | 10.90 | 4.02 | 44.39 | 4.85 |
| c2       | 32.01 | 29.01 | 3.20 | 32.93 | 2.85 |
remarkably with the concentration of HNO₃ increasing from 40 to 120 g l⁻¹, but changed slightly as the concentration of HNO₃ was more than 120 g l⁻¹ in the frequency range from about 100 000 to 0.1 Hz.

Figure 5. Corrosion potential for the test specimens in the mixed solutions of x g l⁻¹ HNO₃ + 25 g l⁻¹ HF at 50 °C.

Figure 6. Nyquist plots for the test specimens in the mixed solutions of x g l⁻¹ HNO₃ + 25 g l⁻¹ HF at 50 °C: (a) x = 40 g l⁻¹, (b) x = 80 g l⁻¹, (c) x = 120 g l⁻¹ and (d) x = 200 g l⁻¹.
The impedance value (i.e., the corrosion resistance) enlarged when the concentration of HNO₃ increased from 40 to 200 g l⁻¹. In particular, a noticeable increase took place from 80 to 120 g l⁻¹ HNO₃. This indicates that the dissolution rate of the specimen becomes slower with the increase of the HNO₃ concentration. In the solutions with no more than 80 g l⁻¹ HNO₃, the passivating effect was weak, especially those under the x < 40 g l⁻¹ conditions that were characterised by a strong metal dissolution (figure 4(a)). The dissolution of oxides and active dissolution of the base metal can easily take place on the surface of the specimen. With the further increase in the concentration of HNO₃, the passivating effect enhanced gradually and resulted in the slow dissolution reactions on the surface of the specimen.

### 3.3. Pickling with different HF concentrations

Figures 8 and 9, and table 3 show the weight loss rates, typical surface images, and EDS analyses after the pickling in the mixed solutions of 120 g l⁻¹ HNO₃ + y g l⁻¹ HF (y = 5 ~ 80) at 50 °C, respectively. The SEM images for y = 25 are shown in figures 4(B) and (b). The weight loss rate increased noticeably and the remaining oxides did not show clear changes in composition when the concentration of HF changed from 5 to 80 g l⁻¹. In the solution with 5 g l⁻¹ HF, the weight loss rate was approximately 0.56 g m⁻² min⁻¹, which was not high enough to efficiently remove the oxide scales from the surface of the specimen. As the concentration of HF changed to 80 g l⁻¹, the weight loss rate showed the highest value at approximately 1.97 g m⁻² min⁻¹ and only a small amount of oxide scales remained on the surface of the specimen. The pickling efficiency of 2205 DSS had a positive correlation with the HF concentration.

![Bode plots for the test specimens in the mixed solutions of x g l⁻¹ HNO₃ + 25 g l⁻¹ HF at 50 °C.](image1)

![Pickling rate for the test specimens in the solutions of 120 g l⁻¹ HNO₃ + y g l⁻¹ HF (y = 5 ~ 80) at 50 °C.](image2)
The corrosion potential in the mixed solutions of 120 g l$^{-1}$ HNO$_3$ $+$ y g l$^{-1}$ HF ($y = 5, 15, 25$ and $80$) at 50 $^\circ$C is shown in figure 10. In the solution with 5 g l$^{-1}$ HF, the corrosion potential was higher than 260 mV$_{MSE}$ and stabilised at about 340 mV$_{MSE}$ after 500 s of immersion. When the HF concentration changed to 25 g l$^{-1}$, the corrosion potential quickly increased from approximately $-150$ mV$_{MSE}$ and attained a relatively steady state at

| Position | O   | Cr  | Mn  | Fe  | Ni  |
|----------|-----|-----|-----|-----|-----|
| a1       | 38.2| 8.36| 3.85| 48.22| 1.37|
| a2       | 35.6| 42.99| 4.65| 15.89| 0.82|
| b1       | 37.1| 9.59| 4.16| 46.42| 2.72|
| b2       | 41.2| 40.49| 2.88| 14.97| 0.38|

Figure 9. SEM surface micrographs and EDS analysis after picking in the mixed solutions of 120 g l$^{-1}$ HNO$_3$ $+$ y g l$^{-1}$ HF at 50 $^\circ$C: (A) $y = 5$ g l$^{-1}$ and (B) $y = 80$ g l$^{-1}$, (a) and (b) are the local magnification areas for (A) and (B).

Table 3. EDS analyses of the marking positions in figure 8 (wt%).

Figure 10. Corrosion potential for the specimens in the mixed solutions of 120 g l$^{-1}$ HNO$_3$ $+$ y g l$^{-1}$ HF at 50 $^\circ$C.
approximately 180 mV$_{MSE}$ with increasing immersion time. Since the HF concentration was higher than 45 g l$^{-1}$, the corrosion potential quickly decreased to the lowest value (lower than approximately $-320$ mV$_{MSE}$) at the beginning of immersion test and then increased slowly to reach a stable value (lower than approximately $-210$ mV$_{MSE}$) when the immersion time increased.

The Nyquist and Bode plots in the mixed solutions of 120 g l$^{-1}$ HNO$_3$ + $y$ g l$^{-1}$ HF ($y = 5, 15, 25$ and $80$) at 50°C under the $E_{corr}$ conditions is shown in figures 11 and 12, respectively. The semicircle size reduced obviously when the concentration of HF changed from 5 to 80 g l$^{-1}$. The phase angle $\theta$ values decreased
remarkably with the concentration of HF increasing from 5 to 80 g l\(^{-1}\) in the frequency range from about 100 000 to 0.1 Hz. In particular, a noticeable reduction took place from 25 to 45 g l\(^{-1}\) HF. These indicate that the higher HF concentration facilitated the dissolution of oxides and base metal, especially under \(y > 25\) conditions (i.e., a transition from the passive state to the active state).

### 3.4. Pickling at different temperatures

Figures 13 and 14 show the weight loss rate and typical surface images after pickling in the mixed solution of 120 g l\(^{-1}\) HNO\(_3\) + 25 g l\(^{-1}\) HF at different temperatures. The SEM images for 50 °C are shown in figures 4(B) and (b). When the temperature changed from 40 to 60 °C, the weight loss rate increased from approximately 0.82 to 1.33 g m\(^{-2}\) min\(^{-1}\). Moreover, the residual oxides became evidently less on the surface of the specimens. The pickling efficiency of 2205 DSS had a positive correlation with the temperature of the solution.
4. Discussion

During pickling in the mixed solutions of HNO₃-HF, HNO₃ acted as the strong oxidant. The low valent oxides can be oxidised into high valent oxides through the chemical reactions (1) to (3). HF has a strong corrosion property. In fact, HNO₃ and HF supply hydrogen ions, which can dissolve the oxides as shown in equations (4) to (7) [18, 35].

\[
\begin{align*}
2\text{FeO} + 2\text{HNO}_3 & \rightarrow \text{Fe}_2\text{O}_3 + 2\text{NO} \uparrow + \text{H}_2\text{O} \\
2\text{Fe}_3\text{O}_4 + 2\text{HNO}_3 & \rightarrow 3\text{Fe}_2\text{O}_3 + 2\text{NO}_2 \uparrow + \text{H}_2\text{O} \\
\text{Cr}_2\text{O}_3 + 6\text{HNO}_3 & \rightarrow 2\text{CrO}_3 + \text{NO}_2 \uparrow + \text{H}_2\text{O} \\
\text{Fe}_2\text{O}_4 + 8\text{H}^+ & \rightarrow 2\text{Fe}^{3+} + \text{Fe}^{2+} + 4\text{H}_2\text{O} \\
\text{Fe}_2\text{O}_3 + 6\text{H}^+ & \rightarrow 2\text{Fe}^{3+} + 3\text{H}_2\text{O} \\
\text{Cr}_2\text{O}_3 + 6\text{H}^+ & \rightarrow \text{Cr}^{6+} + 3\text{H}_2\text{O} \\
\text{MCr}_2\text{O}_4 + 8\text{H}^+ & \rightarrow \text{Fe}^{2+} + 2\text{Cr}^{3+} + 4\text{H}_2\text{O}(M = \text{Fe, Ni, Mn})
\end{align*}
\]

The oxides that remained on the test specimens were Fe₂O₃, Fe₃O₄, MnCr₂O₄, NiCr₂O₄, and FeCr₂O₄ as shown in figure 2. Fe₂O₃ and Fe₃O₄ were the oxides with compact structures, which were difficult to dissolve in most acids [36]. MnCr₂O₄, NiCr₂O₄, and FeCr₂O₄ were the oxides with spinel structures, which were insoluble in the solutions of HNO₃-HF [37]. As seen in tables 2 and 3, after pickling with higher and lower weight loss rates, the remaining oxides did not show clear changes in their composition. The remaining oxides consisted of an outer layer of iron-rich oxides and an inner layer of chromium-rich oxides [29]. The positions a₁, b₁, c₁ in table 2 and a₁, b₁ in table 3 were located in the outer layers which were rather rough with higher Fe content and lower Cr content. The positions a₂, b₂, c₂ in table 2 and a₂, b₂ in table 3 were located in the inner layers which were rather smooth with lower Fe content and higher Cr content. Before and after the different pickling, the structure and composition of the oxides on the test specimens are similar. These imply that the oxides do not readily dissolve during pickling processes.

Most metal elements such as Fe, Cr, Mn, Ni, and Mo in the base metal of 2205 DSS can be dissolved in the mixed solutions of HNO₃-HF through the following chemical reaction:

\[
\text{M} + n\text{H}^+ \rightarrow \text{M}^{n+} + (n/2)\text{H}_2 \uparrow (\text{M = Fe, Cr, Ni, Mn})
\]

The dissolution of base metal can result in the peeling off of the oxide scale. The oxides on the test specimen can also be peeled off by the hydrogen bubbles. It can be assumed that the oxides slowly dissolve and that the pickling efficiency of the DSS 2205 hot-rolled strip can be effectively improved by increasing the dissolution rate of the base materials in the mixed solutions of HNO₃-HF with stronger corrosive properties.

In order to show the dissolution process for the specimens in the mixed solutions of HNO₃-HF at 50 °C, the equivalent circuit models are proposed in figure 15 according to the EIS features in figures 6 and 11 [13, 38, 39].

As shown in figure 6(a), the impedance spectrum consists of a capacitive loop at high frequencies and an inductive loop at low frequencies. The presence of the inductive loop indicates the surface area is partly active. The equivalent circuit for the impedance spectrum is shown in figure 15(a). The impedance Z can be expressed in equation (9) [13].

\[
Z = R_s + \frac{1}{\frac{1}{R_t} + \frac{1}{R_0 + j\omega L} + j\omega C_{dl}}
\]

where \(R_s\) is the solution resistance, including the ohmic resistance of the oxide layer remained on the specimens during pickling. \(R_t\) is the charge-transfer resistance of all electrode reactions taking place in the system, including the intermediate reactions. \(R_0\) is an equivalent resistance. \(L\) is an equivalent inductance. \(\omega\) is the angular
frequency ($\omega = 2\pi f$). $f$ is the frequency applied for impedance measurements. $C_{\text{dl}}$ can be replaced with constant phase element (CPE) [39]. The impedance of CPE is written as equation (10), where $Y_0$ is the admittance magnitude of CPE, $\alpha$ is the exponential term.

$$Z_{\text{CPE}} = \frac{1}{Y_0(j\omega)^\alpha}$$

The parameter of the equivalent circuit are $R_s$ of 16.62 $\Omega$ cm$^2$, $Y_0$ of $9.27 \times 10^{-5}$ S$\Omega^{-1}$ cm$^{-2}$, $\alpha$ of 0.8931, $R_s$ of 75.01 $\Omega$ cm$^2$, $R_t$ of 142.70 $\Omega$ cm$^2$, and $L$ of 60.83 H cm$^2$. The calculated spectra are shown as a solid curve in figure 6(a), which are consistent with the experimental data.

Except figure 6(a), a similar impedance feature is seen from the impedance spectra in figures 6 and 11. In the frequency range of measurement, the Nyquist plots were composed of two depressed semicircles. The high frequency semi-circle expanded with increasing the concentration of HNO$_3$ or decreasing the concentration of HF. The low frequency semi-circle was rather flattened. The equivalent circuit is proposed for the systems in figure 15(b). $R_s$ is the electrolyte resistance. $R_d$ is the resistance of oxide layer remained on the specimens. $R_t$ is the charge transfer resistance. $C_t$ and $C_{\text{dl}}$ can be replaced with constant phase element (CPE). $Z_{\text{dl}}$ is the diffusion impedance, which is written as equation (11) [39].

$$Z_{\text{dl}} = R_d \left( \tanh \left( \frac{j\omega \delta^2}{D} \right) \right)$$

where $R_d$ is the diffusion resistance, $\delta$ is the thickness of the oxide layer, and $D$ is the diffusion coefficient of the electro-active species for cathodic corrosion reaction. Table 4 gives the fitted results of EIS spectra for the test specimens in the mixed solutions of HNO$_3$-HF with different concentrations.

| Solutions g l$^{-1}$ | $R_s$ $\Omega$ cm$^2$ | $Y_0$ S$\Omega^{-1}$ cm$^{-2}$ | $\alpha$ | $R_t$ $\Omega$ cm$^2$ | $Y_{\text{dl}}$ S$\Omega^{-1}$ cm$^{-2}$ | $\alpha_{\text{dl}}$ | $R_d$ $\Omega$ cm$^2$ | $\delta^2/D$ cm$^{-2}$ |
|----------------------|---------------------|------------------------|--------|---------------------|------------------------|--------|---------------------|-------------------|
| 80HNO$_3$ + 25HF     | 14.88               | 2.163E-5               |        | 118.6               | 1.04E-4                |        | 0.7158              | 1415              |
| 120HNO$_3$ + 25HF    | 13.01               | 2.336E-5               | 0.9671 | 411.6               | 6.81E-5                | 0.7352 | 1880               | 1.157E-3          |
| 200HNO$_3$ + 25HF    | 13.11               | 4.158E-6               | 0.936  | 1197                | 2.80E-5                | 0.9999 | 4163               | 4.409E-4          |
| 120HNO$_3$ + 5HF     | 12.9                | 3.326E-5               | 0.9133 | 1604                | 4.20E-5                | 0.815  | 3130               | 7.31E-3           |
| 120HNO$_3$ + 45HF    | 13.18               | 2.87E-5                | 0.9012 | 194.6               | 6.68E-3                | 0.9831 | 10.82              | 0.043 15          |
| 120HNO$_3$ + 80HF    | 13.43               | 2.968E-5               | 0.8802 | 152.7               | 0.008                 | 0.7158 | 47.15              | 0.011 23           |

The calculated spectra are shown as a solid curve in figures 6(b)–(d) and 11, which fit the experimental data very well. It can be concluded that the model provided a reliable description for the corrosion systems.

However, it should be noted that the solutions are corrosive enough that serious intergranular corrosion may occur, as seen in figures 4(a) and 9(b), which can reduce the corrosion resistance and mechanical properties of the product. Therefore, the pickling efficiency and product property should be equally considered. According to the above results, the pickling process of 2205 DSS in the mixed solutions of 120 g l$^{-1}$ HNO$_3$ + 25 g l$^{-1}$ HF at 50°C is in the passive state. In order to improve the pickling efficiency, HF concentration should be more than 45 g l$^{-1}$ and HNO$_3$ concentration should be less than 80 g l$^{-1}$. Moreover, in order to avoid serious intergranular corrosion, HF concentration should be less than 60 g l$^{-1}$ and HNO$_3$ concentration should be more than 60 g l$^{-1}$.

5. Application and performance

The mixed solutions of 60 ~ 80 g l$^{-1}$ HNO$_3$ + 45 ~ 60 g l$^{-1}$ HF at 45 ~ 55°C were adopted in the industrial pickling of 2205 DSS hot-rolled strips. This optimised process markedly enhanced the pickling efficiency with an increase of the pickling speed from 5 ~ 8 m min$^{-1}$ to 15 ~ 18 m min$^{-1}$. In fact, the produced surface finish notably improved, as shown in figure 16.

6. Conclusions

The pickling behaviour of 2205 DSS hot-rolled strip with annealing and sand blasting in the mixed solutions of HNO$_3$-HF has led to the following conclusions:

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Table 4. Fitted results for EIS spectra of the test specimens in different mixed solutions.
The pickling efficiency has a negative correlation with the HNO₃ concentration due to passivation. When HNO₃ concentration is less than 80 g l⁻¹, the pickling rate increases significantly. The pickling efficiency has a positive correlation with HF concentration. When HF concentration is more than 45 g l⁻¹, the active dissolution will noticeably accelerate the pickling process. The pickling rate markedly increases when the temperature of the solution changes from 40 to 60 °C. The pickling process of 60 ∼ 80 g l⁻¹ HNO₃ + 45 ∼ 60 g l⁻¹ HF at 45 ∼ 55 °C is suitable for the industrial production of 2205 DSS hot-rolled strips.

Acknowledgments

Financial support provided by the National Natural Science Foundation of China (Grant No. U1960103 and U1660205) is greatly appreciated.

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Figure 16. Images of 2205 DSS strip after pickling with the optimised process: (a) surface and (b) coil.
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