Oxide Scale Formation of EN 1.4622 and EN 1.4828 Stainless Steels during Annealing and Descaling Behavior in Neutral Electrolytic Pickling

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1. Introduction

Because of their good corrosion and oxidation resistance, formability, and mechanical and physical properties, stainless steels are used in many applications. Examples of the most common usage applications include automotive and transportation, residential, chemical, and petroleum industries.[1] Austenitic stainless steel grades are widely used in high-temperature applications. However, nickel-free ferritic stainless steel has lower thermal expansion coefficient and is cheaper as a material. As such, it has been developed especially for applications with repeated thermal cycles such as automotive exhaust systems.[2–5]

In the industrial manufacturing process, the annealing of cold-rolled stainless steel is performed by a continuous treatment line that has a high temperature, short annealing time, and an oxidizing atmosphere dependent on the fuel and oxidizer used. The annealing is followed by a pickling line. During annealing, an oxide scale layer is formed on the surface of the steel; the thickness and the composition of the oxide scale depend on the annealing conditions and the composition of the steel.[6,7] To restore the corrosion resistance properties of the stainless steel, both the formed oxide scale and the chromium depleted layer below it must be removed. This is usually conducted with sequential electrolytic and mixed acid pickling.[8] Thus, the aim of annealing is to produce the desired microstructure and mechanical properties for the steel[9] in such a way that the material losses are minimized during further processing while ascertaining a good pickling result.[8] This can be achieved by controlling the oxide layer formed on the stainless steel surface to be optimal in terms of thickness and pickling efficiency.

In short-term oxidation studies of ferritic stainless steel, temperatures usually vary between 1000 and 1150 °C, focusing mainly on nonstabilized AISI 430 and dual-stabilized AISI 441 steel grades. Saeki et al.[9] determined that the oxide scale composition of the AISI 430 stainless steel was (Fe,Cr)2O4 after 3 min of oxidation at 1000 °C. In addition, the spinel (Mn,Fe, Cr)3O4 was detected for the same grade with 10 times higher Mn content than in their previous study. When a higher partial pressure of oxygen in the atmosphere is used, the spinel oxide
The differing oxidation behaviors between austenitic and ferritic stainless steels have been compared in several studies. De Carvalho et al.\textsuperscript{[15]} presented that the oxidation resistance of the austenitic AISI 304 is better than that of the ferritic AISI 430. By increasing alloying, ferritic stainless steels have been shown to have higher oxidation and corrosion resistances compared with common austenitic steels. For example, in an oxidizing atmosphere at 950 °C, titanium stabilized ferritic AISI 439 has a better oxidation resistance than AISI 304,\textsuperscript{[16,17]} and ferritic AISI 441 has also been found to have higher corrosion resistance than austenitic AISI 316L at 1100 °C.\textsuperscript{[10]}

In this study, annealing and pickling behavior is compared between two stainless steel grades with suitability for high temperature applications. Austenitic grade EN 1.4828 (AISI 309) has increased contents of chromium and silicon, both of which increase oxidation resistance. Ferritic EN 1.4622 (no AISI equivalent) is a Ti and Nb dual-stabilized, high chromium containing steel grade. High chromium content of ferritic stainless steels elevates their oxidation resistance, and these steels are characterized by a small difference in thermal expansion between the oxide scale and substrate metal which reduces the amount of oxide scale spalling during thermal cycles, prolonging material service life.\textsuperscript{[1]}

For the present steel grades, the literature concerning the oxidation and scale formation is scarce, especially during their manufacturing process conditions. The oxide scale of ferritic EN 1.4622 has been observed to consist of (Mn,Fe)3O4 and Cr2O3 after oxidation for 5 h at 600 °C.\textsuperscript{[18]} Zhixia et al.\textsuperscript{[19]} presented that after long-term oxidation at 1050 °C, the outer layer of the austenitic EN 1.4828 oxide scale consists of FeCr2O4 and NiMn3O4 spinels, the intermediate layer is iron and chromium oxides and the innermost layer is a silicon-rich oxide. Zhan et al.\textsuperscript{[20]} determined that after thermal fatigue test using a 900 °C as the maximum temperature, the oxide scale composition of AISI 309 was Cr2O3, Fe3O4, and Mn1.5Cr1.5O4. Lindell et al.\textsuperscript{[21]} compared hot- and cold-rolled AISI 309L stainless steel annealed in a production line, and their pickling efficiency in mixed acid pickling with HF-HNO3. On the hot-rolled AISI 309L, the formed oxide scale is thicker than on the cold-rolled and consisted of an outer hematite and iron-rich spinel layer, an inner corundum-type chromium-rich oxide layer, and can optionally contain silicon oxide at the metal-oxide interface. On the cold-rolled steel, an outer iron-rich and inner chromium-rich oxide layers could be detected. Both annealed steels are more difficult to pickle than AISI 304L.

The objective of this study is to compare the oxide scale formation of cold-rolled austenitic EN 1.4828 and ferritic EN 1.4622 stainless steels during short-term annealing. The temperature range was 1100–1200 °C for the austenitic and 1000–1100 °C for the ferritic grade, and the annealing was performed using two different atmospheric compositions, low (H2O = 16.1%) and high (H2O = 64.5%) levels of humidity. The composition, structure, and thickness of the oxide scale were determined, and these properties were compared with oxide scale removal efficiency using neutral electrolyte pickling. The results of this study can be utilized in the development of industrial annealing processes for cold-rolled stainless steels toward a more controlled oxide scale formation from the viewpoint of pickling efficiency.

2. Experimental Section

2.1. Annealing Step

Samples of cold-rolled ferritic EN 1.4622 and austenitic EN 1.4828 (AISI 309) stainless steel grades were obtained from the Outokumpu Stainless Oy production line. The chemical compositions of the stainless steels are shown in Table 1. The thickness of the ferritic stainless steel sheets was 1.48 mm and of the austenitic 1.47 mm, and the sheets were cut to 30 × 25 mm² pieces. Annealing was performed in vertical tube furnace for 1, 3, and 5 min using a low water vapor atmosphere and for 5 min using a high water vapor atmosphere. The low water vapor atmosphere simulates CH4 combustion with 20% excess air in the industrial annealing furnace and thus the composition of the atmosphere was set to 72.69% of N2, 16.1% of H2O, 8% of CO2, and 3.22% of O2. The more humid atmosphere simulates an industrial furnace heating using oxygen as combustion gas (Oxyfuel). The composition of the atmosphere is based on CH4 combustion with 5% excess oxygen so that the oxygen concentrations in the atmospheres are similar. The chemical composition of the oxyfuel atmosphere is 64.5% of H2O, 32.3% of CO2, and 3.22% of O2. The atmospheres were formed using a total gas flow of 2 L min⁻¹ into the furnace.

Before annealing, a 2 mm hanging hole was drilled, and the surfaces of the stainless steel samples were cleaned with ethanol. Furnace temperatures of 1000, 1050, and 1100 °C were used for the ferritic and 1100, 1150, and 1200 °C for the austenitic stainless steels annealing. The temperature ranges were selected to

| Steel | C | Cr | Ni | Mn | Cu | Si | N | Other | Fe |
|-------|---|----|----|----|----|----|---|-------|----|
| EN 1.4622 | 0.02 | 21 | – | ≤0.80 | 0.4 | 0.46 | 0.02 | Ti = Nb bal. |
| EN 1.4828 | 0.05 | 19.3 | 11 | ≤2.00 | – | 1.9 | ≤0.11 | bal. |
match the industrially used annealing temperatures of the selected steel grades. The annealing was performed isothermally, and the heating curves of samples were created by moving the sample along with a thermocouple through different temperature zones of the furnace. Examples of heating curves using the minimum and maximum furnace temperatures of both steel grades are shown in Figure 1. Annealing conditions and the maximum temperatures of samples achieved are shown in Table 2.

Table 2. Maximum temperature of samples under certain annealing conditions.

| Steel grade | Sample | $T_{\text{max}}$ of the sample [$^\circ\text{C}$] |
|-------------|--------|----------------------------------|
| EN 1.4622   | F-1000-1-L | 972.3                           |
|             | F-1000-3-L | 983.1                           |
|             | F-1000-5-L | 987.0                           |
|             | F-1000-5-H | 986.9                           |
|             | F-1050-1-L | 1018.9                          |
|             | F-1050-3-L | 1025.7                          |
|             | F-1050-5-L | 1030.6                          |
|             | F-1050-5-H | 1031.4                          |
|             | F-1100-1-L | 1071.1                          |
|             | F-1100-3-L | 1077.9                          |
|             | F-1100-5-L | 1079.4                          |
|             | F-1100-5-H | 1084.7                          |
| EN 1.4828   | A-1100-1-L | 1079.5                          |
|             | A-1100-3-L | 1087.4                          |
|             | A-1100-5-L | 1093.4                          |
|             | A-1100-5-H | 1095.5                          |
|             | A-1150-1-L | 1132.9                          |
|             | A-1150-3-L | 1135.6                          |
|             | A-1150-5-L | 1137.1                          |
|             | A-1150-5-H | 1145.8                          |
|             | A-1200-1-L | 1182.0                          |
|             | A-1200-3-L | 1182.1                          |
|             | A-1200-5-L | 1184.1                          |
|             | A-1200-5-H | 1187.6                          |

$F$ = ferritic, $A$ = austenitic—furnace temperature ($^\circ\text{C}$)—exposure time (min)—low/high H$_2$O atmosphere.

Element depth profiles and the thickness of oxide scales were determined using glow discharge optical emission spectroscopy (GDOES). The oxygen content decreases on the surface toward the steel matrix, and the point of 5 wt% was used to determine the oxide scale thickness from the GDOES profile.[20,21] The structure and composition of the oxide scales were analyzed from cross sections by field emission scanning electron microscopy (FESEM; Sigma Ultra Plus) and energy dispersive spectroscopy (EDS).

2.2. Pickling Step

The annealed samples were pickled using a neural electrolyte pickling device in 17 wt% sodium sulfate (Na$_2$SO$_4$) electrolyte, a current density of 64 mA cm$^{-2}$, a total galvanostatic anodic polarization time of 40 s, and the temperature of electrolyte was between 50 and 55 $^\circ$C with an average temperature of 54 $^\circ$C. The pickling was performed with two titanium (grade 1) electrodes as counter electrodes on both sides of the sample, with working electrodes at 15 mm distances from the sample surface. The used power source and recorder of the current and potential was Keysight E36312A (Keysight, Malaysia). More detailed information on annealing and pickling methods, and schematic figures of annealing and pickling devices are presented in a previous study.[22]

After pickling, the amount of oxide-free and oxide-covering sample surface was examined by FESEM-EDS. The efficiency of pickling was evaluated visually classifying pickling results and by image analysis from FESEM images. These methods, including, e.g., binarization of 8-bit grayscale FESEM images, were based on our previous study.[22] The image analysis was used to compare the thickness of the oxide scale formed during annealing and the pickling efficiency, and to assess the separability of the visual classification.

3. Results

3.1. Characterization of Oxide Scale

3.1.1. Austenitic EN 1.4828

The cross-sectional structures, backscattered electrons (BSE) images, of annealed EN 1.4828 surfaces' structure, EDS element composition maps, and EDS point analyses are shown in
Figure 2 and 3. The elemental contents from EDS points analyses in FESEM BSE images are shown in Table 3. Figure 2 and 3 show that silicon oxide is detected as dark areas in all of the FESEM images taken from the annealed surfaces' cross sections. Silicon oxide is formed below the metal-oxide interface penetrating toward the steel matrix which is seen in the micrographs as a light gray tonality. An uneven surface due to angular pieces at the sample-epoxy (epoxy seen as black) interface is observed after 1 min annealing at 1100 and 1150 °C. The uneven surface is shown in Figure 2a, and EDS point 1 in Table 3 shows that, containing no oxygen, the angular pieces are of the steel matrix. These steel matrix pieces are not observed as the annealing time increases, and as shown in Figure 2b, the surface remains relatively smooth. Based on the EDS maps of elements in Figure 2c, the oxide scale layer on the surface consists mainly of chromium-rich oxide. In addition, small amounts of manganese are detected in the layer, and silicon oxide areas are observed in connection with the layer as well as in the matrix. Thicker layers of chromium-rich oxide are formed after 5 min in both atmospheres, as shown in Figure 2d,e.

As shown in Figure 3a,b, the thickening of the chromium-rich oxide is detected at 1200 °C, and composition of this oxide layer is presented at point 2 in Table 3. An iron rich-oxide is observed to form on surfaces annealed for 5 min in both atmospheres, as shown in Figure 3c,d. EDS map analysis of a formed oxide nodule from Figure 3c is present in Figure 3e, and on that basis the upper part of the nodule consists mainly of iron oxide. In addition, the lower part is enriched with chromium and small parts of nickel and silicon. The result of elemental points from the nodule formed in high water vapor atmosphere (in Figure 3d) is shown in Table 3, and it supports the previously observed structure of an upper iron oxide part, as seen in point 3. The middle part of the nodule, at point 4, consists of a chromium- and iron-rich oxide. The inner part of this chromium- and iron-rich oxide is enriched with nickel, as shown at point 5. In addition, when comparing the amount of oxide nodules in different atmospheres, as shown in Figure 3f,g, it was found that a higher proportion of water vapor in the atmosphere produces significantly more oxide nodules. Thus, the amount of water vapor was found to have an accelerating effect on oxidation. A summary of the structural properties of the oxide scales and their thicknesses as measured by GDOES is shown in Table 4.

The GDOES elemental depth profiles of EN 1.4828 are shown in Figure 4, where the yellow vertical line represents the oxide-metal interface with oxide to the left of the line and metal substrate to right. These elemental profiles showed that the main metallic element of oxide scales is chromium, and even in the weakest annealing condition, at 1100 °C for 1 min in low water vapor atmosphere, the formation of sublayers can be observed in the chromium oxide layer. The outermost layer is enriched with manganese and iron, the middle layer contains chromium and iron in different ratios after different annealing conditions, and the innermost layer is enriched with silicon. The oxide scales are usually free of nickel, but after the nodule formation, nickel enrichment is observed in the lowest parts of the nodules.

The oxidation of stainless steel grade EN 1.4828 causes a chromium depleted layer below the oxide layer which can be detected in the GDOES depth profiles from the decrease in chromium content before settling to the level. The depth of this chromium depleted layer from the surface depends on the annealing conditions in such a way that a longer annealing time and a higher temperature causes Cr-depleted layer and bulk steel interface to shift deeper into steel matrix.
3.1.2. Ferritic EN 1.4622

The thin oxide layers consisted of mainly chromium-rich oxide, but separate sublayers from the chromium-rich oxide layer for each annealed surface were present regardless of the annealing conditions. Manganese and iron are enriched at the gas-scale interface, the highest chromium content of oxide scale is halfway through the oxide layer, and silicon is enriched at the oxide–metal interface, as seen in the GDOES depth profiles in Figure 5. The formation of the chromium depleted layer is much lower than in EN 1.4828, and not observed at all locations throughout the cross section.

BSE cross sections of the surfaces of stainless steel grade EN 1.4622 annealed for 5 min at 1050 °C in low humid atmospheres and 1100 °C in both humid atmospheres are shown in Figure 6. The initial formation of nodules in the ferritic grade begun at 1050 °C after 3 min and was seen in higher quantities after 5 min of annealing. Below these small nodules, dark silicon oxide areas are detected which are marked by red arrows in Figure 6a. At 1100 °C, large nodules of oxide have formed on the surface in both atmospheres (Figure 6b,c), and the nodules are constructed of smaller oxide pieces. The elemental composition of the nodules was mainly chromium oxide and below them at the oxide–metal interface was an oxide area enriched in silicon. The light areas inside the oxide scale may be enriched with iron and niobium, and some enrichment of titanium was detected in the steel matrix as seen in EDS maps in Figure 6d. The composition of EDS point 6 in Figure 6b is shown in Table 3, showing that small amounts of titanium and niobium were found in the nodule. A summary of thickness and structural properties of the ferritic EN 1.4622 oxide scales is shown in Table 4.

Table 3. Elemental contents of EDS points 1–6 from Figure 2, 3, and 6, in wt%.

| Point | Fe   | Cr  | Ni  | O   | Si  | Mn  | Ti  | Nb  | Tot. |
|-------|------|-----|-----|-----|-----|-----|-----|-----|------|
| 1     | 62.3 | 17.0| 10.9| 1.2 |     |     |     |     | 91.4 |
| 2     | 7.0  | 49.4| 0.7 | 25.3| 0.6 | 2.2 |     |     | 85.2 |
| 3     | 59.5 | 1.7 |     | 23.6|     |     |     |     | 84.8 |
| 4     | 25.8 | 28.4| 1.5 | 27.2| 2.0 |     |     |     | 84.9 |
| 5     | 16.7 | 30.8| 12.4| 21.4| 1.0 | 1.3 |     |     | 83.6 |
| 6     | 3.0  | 61.3| 29.3| 0.4 | 0.4 | 0.8 |     |     | 95.2 |

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3.2. Electrolytic Pickling

From FESEM images of pickled surfaces, the efficiency of pickling was evaluated visually and by image analysis. The visual evaluation was performed by classifying the pickled surfaces into four categories: excellent (4), good (3), decent (2), and bad (1) and calculating the average for the images of the same sample to describe the pickling efficiency. An excellent result is provided on the sample surface where most of the surface is oxide-free. A good result means that approximately half of the surface is oxide-free. In a decent result, the pickled surface remains covered by scale, but areas of chromium depleted layers are revealed and in bad result, the surface is completely covered with oxide. Examples of these categories are shown in Figure 7.

The visually evaluated results of neutral electrolytic pickling efficiency are shown in Table 5 and 6. The tables show how the four analyzed images from each sample are divided into pickling categories, and how the average scores of pickling efficiencies are based on a score ranging from 4 to 1.

For ferritic steel grade EN 1.4622, half of the pickled samples got an average score over 3, meaning that the pickling efficiency of these samples is at least good. These categories include all the samples at the lowest temperature and samples with an annealing time of 1 min. The pickling results of the other half of the samples were weaker and the pickling efficiency approaches a bad result when the exposure time was increased at 1050 and 1100 °C. For austenitic grade EN 1.4828, only two samples, A-1100-1-L and A-1150-1-L, had a pickling result other than bad.

The amount of current needed for dissolution of the scale was estimated using Equation (1)

\[
Q_{req} = \frac{dFz}{pV_m}
\]

where \(d\) is the measured thickness of the scale, reported in Table 4, \(F\) is the Faradays constant, \(z\) is the number of electrons transferred when chromium oxide reacts with water: \(6, [21, 24]\) \(p\) is the current efficiency of the reaction, estimated to be 0.1, \([21,24]\) and \(V_m\) is the molar volume of the chromium (III) oxide, 29.12 cm\(^3\) mol\(^{-1}\). The calculated values are compared with total current inserted to the system (\(Q_{total}\)) 2.56 As cm\(^{-2}\) and shown in Table 5 and 6.

### 3.3. Associating Experimental Results with the Image Analysis

#### 3.3.1. The Rate of Scale Growth and Its Effect on the Observed Pickling Efficiency

The evolution of the scale thickness during annealing as a function of temperature and time was described using a kinetic analysis taking the parabolic rate law as the basis function. The guidelines followed the recommendations for the model fitting
procedure given in Vyazovkin et al.\textsuperscript{[25]} The parabolic rate law assumes that the diffusion of the oxidizing compound through the growing oxide layer limits the rate of scale formation.\textsuperscript{[26]} In the parabolic rate law, the rate of the oxide scale growth is reciprocal to its thickness at time instant $t$, given as Equation (2)

$$\frac{d\xi}{dt} = \frac{k}{\xi_t}$$  \hspace{1cm} (2)

where $\xi$ is the scale thickness in meters and $k$ is the apparent parabolic rate constant ($m^2 \text{s}^{-1}$) for the scale growth during oxidation. The integral form of the law is given as Equation (3)

$$\xi_t = \sqrt{kt}$$  \hspace{1cm} (3)

The $k$ can be solved for each temperature using the method of least squares. Assuming that the temperature dependency of the rate constant follows the Arrhenius type relation, the temperature dependence of it can be given as Equation (4)

$$k = A_0 \exp\left(\frac{-E_A}{RT}\right)$$  \hspace{1cm} (4)

where $E_A$ is the apparent activation energy, $A_0$ is the frequency factor, $R$ is the molar gas constant, and $T$ is the temperature in Kelvins. The apparent activation energy can be obtained with the method of least squares between the logarithmic form of the Arrhenius law and the natural logarithm of the apparent rate constant. With this procedure, the apparent activation energy computed based on the parabolic rate law for the Ferritic grade was 507.5 kJ mol$^{-1}$ and for the Austenitic grade 308.1 kJ mol$^{-1}$. The Arrhenius plot for both steel grades is shown in Figure 8. Further analysis of the scale growth for the ferritic grade revealed that it
does not strictly obey the parabolic time law for the higher temperatures \( (R^2 \approx 0.88 \text{--} 0.93) \), resulting in the biased activation energy because of the obscure mechanism. In fact, the dependence between scale thickness and time at higher temperatures seems rather linear, which indicates that there is no diffusion control. However, a more detailed investigation of the reaction mechanism is needed with a larger data set that allows the use of model free methods, or to statistically compare several kinetic mechanisms using the model fitting method \([25]\). This is of great interest in future studies. Regardless of the exact activation energy values, the scale growth rate was well explained because the parameterization of the rate law with respect to both the frequency factor and activation energy compensates for the inaccurate mechanism \([25]\).

The estimated scale thicknesses were then associated with features computed from the grayscale FESEM images. The feature set consisted of some basic image features, such as mean, median, variance, and quantiles of intensities, and some more advanced features such as Shannon’s entropy, binarized gradient magnitude, and fractions of pixels in a segmented image using multithreshold Otsu’s segmentation \([27]\). To exemplify the procedure, the computed Shannon’s entropy values are presented as a function of the computed scale thicknesses in Figure 9. From the figure it can be seen that the observed entropy of the pickled sample surface images correlates well \( (R^2 = 0.72) \) with the estimated scale thickness formed during the annealing.

The reasoning behind this can be further associated with the definition of the entropy. Using In-basis, Shannon’s entropy \([28]\) for a grayscale image can be given as Equation (5)

\[
H(X) = - \sum_{i=0}^{255} P(X_i) \ln(P(X_i))
\]

where \( P(X_i) \) is the dot probability of an intensity value \( i \) in image \( X \) estimated from the intensity histogram and \( H(X) \) is the entropy of image \( X \). The entropy is maximized in a system where
a complete disorder prevails. A disordered system is analogous to an image where each of the image pixel values is equally probable. To exemplify this, the entropy for Figure 7a (Excellent) is lower than for Figure 7c (Decent). On the contrary, a homogeneous image is to some extent ordered, or to put it in another way, there are a very few different pixel values, and consequently the grayscale histogram has a distinct local maximum or maxima. Coupling the definition with the scaling, heterogeneity in the scale layer results in a high entropy, whereas a well-pickled surface is quite homogeneous, and consequently has a lower entropy. Furthermore, as it is assumable that the scale thickness is a major factor that determines the pickling efficiency, the correlation seems rather causal. Interestingly, the same correlation was observed only with the austenitic grade, as for the ferritic steel, the entropy of the image decreases after the temperature in the annealing is over 1050 °C and the holding time is over 3 min, consequently resulting in a homogeneous looking scale. This might indicate that there are other properties in the formed scale that influence the scale morphology and thus the pickling result. One factor could be the phase composition of the scale. These properties could be of very high interest in future studies.

Figure 6. BSE cross sections of EN 1.4622 surfaces: a) F-1050-5-L, b) F-1100-5-L, c) 1100-5-L, and d) EDS maps of part b.

Figure 7. Examples of the classification of the pickling results: a) F-1000-1-L (excellent), b) F-1000-5-L (good), c) F-1050-3-L (decent), and d) F-1100-5-L (bad).
Table 5. Pickling efficiency of austenitic EN 1.4828.

| Sample      | Excellent | Good | Decent | Bad | Average score | Q_m/Q_m |
|-------------|-----------|------|--------|-----|---------------|---------|
| A-1100-1-L  | 4         | –    | –      | 4   | 3.98          | 0.64    |
| A-1100-3-L  | –         | –    | 4      | 1   | 9.34          | 0.27    |
| A-1100-5-L  | –         | –    | 4      | 1   | 13.12         | 0.20    |
| A-1100-5-H  | –         | 3    | –      | 1   | 13.72         | 0.19    |
| A-1150-1-L  | –         | –    | 4      | 1   | 15.31         | 0.17    |
| A-1150-5-L  | –         | –    | 4      | 1   | 20.68         | 0.12    |
| A-1150-5-H  | –         | –    | 4      | 1   | 22.86         | 0.11    |
| A-1200-1-L  | –         | –    | 4      | 1   | 8.15          | 0.31    |
| A-1200-3-L  | –         | –    | 4      | 1   | 22.67         | 0.11    |
| A-1200-5-L  | –         | –    | 4      | 1   | 31.41         | 0.08    |
| A-1200-5-H  | –         | –    | 4      | 1   | 37.98         | 0.07    |

Table 6. Pickling efficiency of ferritic EN 1.4622.

| Sample      | Excellent | Good | Decent | Bad | Average score | Q_m/Q_m |
|-------------|-----------|------|--------|-----|---------------|---------|
| F-1000-1-L  | 4         | –    | –      | 4   | 2.78          | 0.92    |
| F-1000-3-L  | 4         | –    | –      | 4   | 2.78          | 0.92    |
| F-1000-5-L  | 1         | 3    | –      | –   | 3.25          | 0.61    |
| F-1000-5-H  | 3         | 1    | –      | –   | 3.75          | 0.50    |
| F-1050-1-L  | 4         | –    | –      | 4   | 2.39          | 1.07    |
| F-1050-3-L  | –         | 1    | 3      | –   | 2.25          | 0.96    |
| F-1050-5-L  | –         | –    | 3      | 1   | 1.25          | 0.56    |
| F-1050-5-H  | –         | –    | 3      | 2   | 1.75          | 0.33    |
| F-1100-1-L  | 4         | –    | –      | 4   | 3.18          | 0.80    |
| F-1100-3-L  | –         | –    | 4      | 1   | 15.51         | 0.17    |
| F-1100-5-L  | –         | –    | 4      | 1   | 26.84         | 0.10    |
| F-1100-5-H  | –         | –    | 4      | 1   | 30.22         | 0.08    |

3.3.2. Analysis of Pickling Efficiency Class Separability from Image Data

To investigate the other features that could be used to discriminate the pickling efficiency for both steel grades, a linear discriminant analysis was conducted. In the linear discriminant analysis, the objective is to find a hyperplane that separates the class observations well. For this aim, the class boundaries defined in Table 5 and 6 were discretized so that the samples with a higher average score than 2.5 were associated with class 1, while all others were associated with 0. Then, an exhaustive search was used to identify the best separating 1, 2, ..., N-dimensional hyperplanes. The linear discriminant function is thus defined here as Equation (6)

$$ g(x) = w_i x_i + w_0 $$

where $$ x $$ is a scaled feature vector of the observation $$ i $$, and $$ [w_i; w_0] $$ is the parameter vector of a linear hyperplane. The hyperplane coefficients can be obtained with the method of least squares using the Moore–Penrose inversion[29] as Equation (7)

$$ w = (X^T X)^{-1} X^T y $$

where $$ X $$ is now a scaled and augmented feature matrix. The augmentation means that the first column of $$ X $$ corresponds to the vector of ones. The training vector is constituted of −1 and 1’s, and consequently, the discriminating rule between the classes is presented as Equation (8)

$$ \text{Class} = \begin{cases} \text{good} & \text{if } g(x) > 0 \\ \text{bad} & \text{if } g(x) \leq 0 \end{cases} $$

Due to a small set of images, the $$ N $$ was set to 5. Due to the small data set, the discriminant analysis was not conducted in predictive purposes but is used to identify proper feature descriptors for future studies. For this reason, the use of cross-validation was not considered necessary. The discriminating hyperplanes with corresponding accuracies for the training set are defined in Table 7. The identified discriminant boundary using the mean intensity and fraction of white pixels obtained using Otsu’s multithreshold segmentation are shown in Figure 10. It can be seen from the figure that the identified discriminant boundary separates the good and the bad observations well, indicating that pickling efficiency can be evaluated from the FESEM image of the sample surface. From the figure it can also be seen that if the $$ f_i $$ feature value is high and the image is whiter on average, the sample is more likely to be well pickled. This finding supports the applicability of the formulated quality index, even though denser class boundaries demand more sample images. Furthermore, with a more extensive set of images, a more sophisticated classifier identification procedure and thus a classifier that uses a larger set of features could be formulated.

4. Discussion

4.1. Differences between Austenitic EN 1.4828 and Ferritic EN 1.4622 Oxide Scales

The oxide scale formed on austenitic EN 1.4828 was mainly a thin continuous chromium-rich oxide layer with a considerable
The computations are presented for the Austenitic grade.

The exemplified linear discriminant function separating the data set to well and badly pickled samples.

Table 7. Discriminant functions and the used feature descriptors. The labels denote the feature numbers in the original set and are only used to illustrate the number of selected features for the discriminant function.

| Features | Accuracy | Feature labels | Feature labels |
|----------|----------|----------------|----------------|
| 1        | 0.82     | −1.3846, 2.2279| 8              |
| 2        | 0.86     | −1.035, −1.219, 3.378| 13, 24         |
| 3        | 0.87     | −0.639, 12.41, 2.707, −13.909| 1, 8, 19       |
| 4        | 0.88     | −0.5839, 40.96, 2.528, 129.6, −171.6| 1, 8, 18, 19   |
| 5        | 0.90     | 1.73, −2.83, 3.76, 1.64, −4.79, 1.83| 7, 8, 12, 13, 14|

The oxide nodules of ferritic grade were also different than austenitic grade because they consisted mainly of chromium oxide with internal iron and niobium enriched metallic small particles, and no iron oxide or any oxide penetration under nodules toward the steel matrix was detected. It is possible that the metallic particles could be similar inclusions whose formation mechanism on the ferritic bistabilized grade 441 has been studied by Issartel et al.[30–32] Based on the mechanism, the metallic inclusions are trapped into the chromium-rich oxide due to silicon oxide layer formation on the metal-oxide interface, and these inclusions oxidize and, thus, disappear from the oxide layer over the annealing time. Correspondingly, the nodules formed on grade EN 1.4622 had a similar element structure than in the nodules on grade 441 formed during longer oxidation periods because oxidized iron was not part of the basic structure of the nodules and the presence of niobium and titanium was observed.[33,34]

The oxidation resistance comparisons between the steel grades used in this research are based on the thicknesses of the oxide layers and the formation of iron oxide which may indicate the onset of breakaway oxidation. Therefore, the ferritic grade has better oxidation resistance than austenitic in their corresponding annealing temperature ranges. The better oxidation resistance of ferritic EN 1.4622 than austenitic EN 1.4828 may be the result of greater chromium diffusivity in the ferritic versus the austenitic structure[10,35] because the higher diffusion rate of chromium can promote chromium oxide layer repair and thus help maintain its protection. The previous study focused on oxide scale formation on austenitic AISI 304 oxidized in the same low water vapor annealing conditions as EN 1.4828.[22] In the most demanding conditions, i.e. in five minutes at 1200 °C, the oxide layer and a net-like-structured under layer due to breakaway oxidation, and the total thickness of oxide was over 30 μm. Based on these results, in their respective heating conditions the oxidation resistance of EN 1.4828 is better than the low alloyed AISI 304, as is to be expected.

From all GDOES depth profiles of both austenitic and ferritic grades, silicon enrichment at the oxide–metal interface was...
observed. However, the amounts and locations of silicon oxide formation are different between the steel grades. Silicon alloying was lower in the ferritic grade (0.6%) than it was in the austenitic (1.9%), and the amount of formed silicon oxide during annealing was also significantly lower in the ferritic grade, as shown in Figure 11. The silicon oxide more clearly formed a continuous layer on the oxide–metal interface in the ferritic grade (Figure 11a,b), and the oxidation of silicon was more internal and intergranular in the austenitic grade, as shown in Figure 11c,d.

The steel matrix pieces on the uneven surface of austenitic samples A-1100-1-L and A-1150-1-L were probably due to cracking after the silicon oxide having formed on the lateral grain boundary. The lateral intergranular oxidation of silicon is marked on Figure 11c. This kind of oxidation can lead to cracking on the silicon oxide–metal interface likely during cooling. At longer annealing times, no cracking of the matrix is observed, so it is likely that the surface is leveled according to the tops of the granules. Spalling behavior of austenitic stainless steel is reported to be possible to occur both on the chromium oxide–silicon oxide and the silicon oxide–metal interfaces.\[36\]

Differences in the locations of silicon oxides may be the result of different diffusion rates in steel grades, in which case the diffusion rate of silicon in the austenitic grade would not be sufficient to produce a continuous layer. Similarly, Nguyen et al.\[35\] observed that the lower diffusion rate of silicon in austenitic Fe–20Cr–20Ni–0.2Si alloy produced discontinuous silicon oxide layer while continuous layer formed in ferritic Fe–20Cr–0.2Si alloy. The differences in locations may also be due to the silicon contents of steel grades. Evans et al.\[36\] presented that a continuous silicon oxide layer is not formed when the silicon content of the Fe–20Cr–25Ni stainless steel is 1.56% or higher. However, Basu and Yurek\[37\] observed that a higher silicon content and smaller grain size promote the formation of a continuous layer in Fe–18Cr–20Ni alloy, and they reported a Si content requirement of 1.5% while 0.6% was too low. The grain boundaries are great diffusion channels toward the oxide–metal interface, so a small grain size promotes the lateral growth of silicon oxide due to the grain boundaries being closer to each other.

A continuous silicon oxide layer is a diffusion barrier which prevents diffusion of Cr and Fe cations from the steel matrix toward the surface and the diffusion of oxygen anions from the atmosphere toward the steel matrix.\[16,38\] Thus, a continuous silicon oxide layer is more protective than a discontinuous one which can promote the formation of iron containing nodules above discontinuous areas.\[35\]

4.2. Differences between Water Vapor Contents in the Formation of Oxide Scales

The effects of low and high water vapor contents were compared with 5 min exposure times in annealing. The oxides formed on the austenitic and ferritic grades were all very slightly thicker after annealing in high water vapor content and only the highest furnace temperature in annealing for both grades produced a greater difference between the thicknesses. For the austenitic grade, the difference between the oxide thicknesses of low and high water vapor content was 0.33 μm at 1200 °C and for the ferritic grade 0.17 μm at 1100 °C.

The difference in oxide scale structures in the austenitic grade is clear at 1150 °C because the formation of nodules only occurs at the high water vapor atmosphere, as shown in Table 4. The higher content of water vapor in the atmosphere also produced more nodules on surfaces annealed at 1200 °C, and thus water vapor is found to have an accelerating effect on the oxidation of grade EN 1.4828. However, these kinds of structural differences in oxide scales are not observed between atmospheres in the ferritic grade.

The accelerating effect of water vapor, which produces a thicker oxide and more iron oxide during high-temperature oxidation, has been reported in several studies.\[10,11,39–41\] In these the effect of humidity was studied mainly in atmospheres with less than 20% water vapor. Lindell et al.\[42\] have studied water vapor containing atmospheres by burning propane using air or oxyfuel burners, which corresponds to water vapor contents of 15% and 57%. These different atmospheres did not produce a difference between the oxide scales formed on AISI 304 in the used short annealing times of under 120 s.

4.3. Effect of Formed Oxide Scale on Electrolytic Pickling Efficiency

The oxide scales of the ferritic grade EN 1.4622 had a considerably better electrolytic pickling efficiency than the oxide scales of the austenitic grade EN 1.4828 when the steels’ own strip manufacturing annealing temperature ranges were used for producing oxide during annealing. In addition, the change in annealing conditions toward more challenging conditions divided the ferritic pickling results more evenly between excellent and bad than the austenitic pickling results. Unlike with the ferritic samples, the pickling efficiency of the austenitic samples dropped significantly, when the oxide scale thickened using annealing times longer than 1 min or the annealing temperature of 1200 °C.

Figure 11. BSE cross sections of annealed surfaces: a) F-1050-3-L, b) EDS maps of part a, c) A-1150-3-L, and d) EDS maps of part (c).
Comparing the evaluated pickling results with the thicknesses of the oxide scales, it was found that ferritic oxides that produce completely bad pickling results, with an average value of 1, are at least 0.78 μm thick. This indicates that the electricity introduced was not enough to dissolve the scale to the extent that would be required. Therefore, the thickness of the oxide layer is the first factor that influences the pickling result. Almost all ferritic oxide layers are quite thin, and in general, a thinner chromium-rich oxide layer is easier to remove from the surface. For example, Hildén et al.\textsuperscript{[23]} proved that the progression of dissolution over time makes chromium-rich oxide layer thinner by electrolytic pickling. The uncertainty of the current efficiency of the dissolution reaction, that is the part of current used to dissolve the oxide phase, makes it difficult to calculate the total amount of electricity required to fully dissolve the oxide phase. The results correlate with the expected relation between electricity inputted into the system and the electricity required. Thus, electrolytic pickling efficiency could be increased by increasing pickling time in the ferritic grade. In austenitic grade, the bad pickling results were observed with an oxide scale thickness of only 0.41 μm which is thinner than the corresponding ferritic oxide scale thickness limit for a bad pickling result. But unlike with the ferritic grade, the high silicon oxide content of the austenitic grade suggests that a higher current density is not likely to improve electrolytic pickling results.

The second factor for the differences in pickling results between the ferritic and austenitic steel grades is the composition and structure of oxide scales based on the electrolytic pickling mechanism. The chromium-rich oxide layer of ferritic EN 1.4622 was similarly layered as in the EN 1.4828: an Mn and Fe enriched surface layer, a chromium-rich middle layer, and a Si enriched inner layer. The dissolution of chromium and manganese oxide is preferred over iron oxide while the dissolution of silicon oxide is nonexistent in neutral electrolytic pickling.\textsuperscript{[23]} The uncertainty of the current efficiency of the dissolution reaction, that is the part of current used to dissolve the oxide phase, makes it difficult to calculate the total amount of electricity required to fully dissolve the oxide phase. The results correlate with the expected relation between electricity inputted into the system and the electricity required. Thus, electrolytic pickling efficiency could be increased by increasing pickling time in the ferritic grade. In austenitic grade, the bad pickling results were observed with an oxide scale thickness of only 0.41 μm which is thinner than the corresponding ferritic oxide scale thickness limit for a bad pickling result. But unlike with the ferritic grade, the high silicon oxide content of the austenitic grade suggests that a higher current density is not likely to improve electrolytic pickling results.

The usual single-pass process route includes first the electrolytic pickling, followed by the mixed acid pickling. The mixed acid pickling is required for the removal of the remaining oxides, especially silicon oxide, and the chromium depleted layer.\textsuperscript{[8,23,43]} In the austenitic oxide scale, the formation of the iron oxide, the internal oxidation below the nodules, and the silicon oxide inside the steel matrix are problematic for the success of the pickling process. These reduce the uniformity of the steel surface and in the final pickling, sufficient surface material must be removed to produce a clean and flawless surface for the final product.

The high chromium concentration of the metal layer beneath the oxides not only slows the final mixed acid pickling,\textsuperscript{[20]} but also reduces the material loss as the chromium depleted layer is significantly thinner. Chromium depletion is greater in the austenitic grade compared with the ferritic, increasing dissolution speed during mixed acid pickling. However, this depletion layer extends to a depth of several micrometers, which also causes the need to remove more material from the austenitic surface. In addition, there are silicon oxide penetrations in the austenitic steel matrix at depths of up to 10 μm, which may increase the amount of surface material removed.

5. Conclusion

The oxide scale formation of ferritic EN 1.4622 and austenitic EN 1.4828 stainless steels was studied in simulated short-term industrial annealing at temperatures between 1000 and 1100 °C for the ferritic and 1100 and 1200 °C for the austenitic grade in atmospheres containing low (16.1%) and high (64.5%) amounts of water vapor. Significant differences in the elemental composition and the structure of the resulting oxide scales were found between the steel grades. The ferritic scales were mainly thin chromium-rich oxides without iron oxide formation in all studied characteristic annealing conditions. The austenitic scales were slightly thicker chromium-rich oxides with a high amount of silicon oxide that penetrated deep into the steel matrix in all the studied annealing conditions and have iron oxide containing nodules in more demanding annealing conditions. Thus, the increase in annealing temperature and time have a higher effect on oxide thickness for the austenitic steel grade than for the ferritic steel grade in the steels’ own annealing temperature ranges. The water vapor content had only a minor influence on the thickness of the formed oxide scale layers. For the austenitic steel grade, increased H₂O content caused an increase in the number of nodules and nodule formation at lower temperature.

The neutral electrolytic pickling efficiencies for the resulting oxide scales were compared between steel grades, and based on the results, the ferritic grade EN 1.4622 oxide scales are better suited for removal by electrolytic pickling than the austenitic EN 1.4828 oxides. A significant proportion of ferritic oxide scales had pickling results between excellent and decent, while only two of the austenitic oxide scales fall into these categories. It was also found that the pickling efficiency and the effect of the formed oxide scale could be observed from images of the pickled surfaces. A more comprehensive data set could thus offer a baseline for an image based pickling quality classifier.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

annealing, cold-rolled stainless steel, electrolytic pickling, oxide scale
